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GRANULAR OPTICAL MATERIALS

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28 February 1978

FINAL REPORT
For the period 1 January 1975 to 31 December 1977

Contract No. F44620-75-C-0057

Prepared for
AIR FORCE OFFICE OF SCIENTIFIC RESEARCH
Washington, DC 20332

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM	
1. REPORT NUMBER AFOSR-TR-78-0714	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER	
4. TITLE (and Subtitle) GRANULAR OPTICAL MATERIALS.	5. TYPE OF REPORT & PERIOD COVERED Final Report (1-1-75 to 12-31-77)		
6. AUTHOR(s) J. Gittleman E. K. Sichel	7. PERFORMING ORG. REPORT NUMBER PRRL-78-CR-8		
9. PERFORMING ORGANIZATION NAME AND ADDRESS RCA Laboratories/ Princeton, New Jersey 08540	8. CONTRACT OR GRANT NUMBER(s) F44620-75-C-0057		
11. CONTROLLING OFFICE NAME AND ADDRESS Air Force Office of Scientific Research Bolling Air Force Base / NE Washington, DC 20332	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 61102F 2306C2		
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)	12. REPORT DATE February 1978		
	13. NUMBER OF PAGES 58		
	15. SECURITY CLASS. (of this report) Unclassified		
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE N/A		
16. DISTRIBUTION STATEMENT (of this Report) <div style="border: 1px solid black; padding: 5px; text-align: center;"> DISTRIBUTION STATEMENT A Approved for public release; Distribution Unlimited </div>			
17. DISTRIBUTION STATEMENT (for the abstract entered in Block 20, if different from Report) <div style="border: 1px solid black; padding: 5px;"> Final rept. 1 Jan 75-31 Dec 77, </div>			
18. SUPPLEMENTARY NOTES			
19. KEY WORDS (Continue on reverse side if necessary and identify by block number)			
Optical properties	Selective absorption	Immiscible	Au-MgO
Plasma frequency	Cermets	systems	Au-WO ₃
Maxwell-Garnett	Granular metals	Electrochromic	Tungsten
Effective Medium Theory	Composite systems	Si-CaF ₂	bronze
20. ABSTRACT (Continue on reverse side if necessary and identify by block number)			
<p>The research under this contract has been directed mainly toward the understanding of the optical behavior of those composite materials whose components are separated on a scale that is very small ($\leq 100 \text{ \AA}$) compared with the wavelength of light. In the course of this work two types of new materials have been developed: (1) semiconductor-insulator composites which may be valuable as selective absorbers of solar</p>			

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radiation in solar thermal applications, and (2) electrochromic cermets which may have applications in a variety of display devices. Comparison of the predictions of two theories -- the Maxwell-Garnett theory (MG) and the effective-medium theory -- with the observed optical behavior of cermets formed by cosputtering a metal and an insulator clearly favored the MG theory. The optical properties of most Au, Ag, and W cermets were at least qualitatively described by MG, and good quantitative agreement could be obtained in most cases by modifying the published values of the optical constants of the metals to take into account the very short electron-scattering times found in the cermets. The most notable exception was Au-MgO, which did not exhibit the dielectric anomaly observed in most other Au cermets at wavelengths accurately predicted by MG. In the case of Au-MgO it was felt that observed surface texturing was dominating its optical behavior. Further, the wavelength at which the SiC Reststrahlen absorption occurred was found to be a function of Si concentration in Si-SiC composites and was accurately predicted by MG. Si-CaF₂ and Si-MgO composites behaved as expected except for an anomalous absorption appearing near 12 μ m. This could be due to chemical reaction involving the silicon and the insulator.

Au-WO₃ is an electrochromic cermet. Like other insulator-rich cermets, it is an insulator at absolute zero and has a conductivity that obeys the characteristic $\exp(-aT^{-1/2})$ law both in its colored and uncolored states. Further, the uncolored cermet is blue turning pink when electrochemically colored due to a shift in the dielectric absorption anomaly from 6000 to 5500 Å. This is quite different from pure WO₃ which is transparent and insulating uncolored and becomes blue and conducting upon coloring. The blue appearance of pure WO₃ is due to a broad absorption in the red and infrared which is associated with the conduction electrons.

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I. SUMMARY

A. INTRODUCTION

The research during the first two years of the contract (January 1975 - December 1976) concentrated on the optical properties of a number of composite materials and the comparison of these values with the predictions of the Maxwell-Garnett theory. In addition, a new, optically active material, an electrochromic cermet, cosputtered Au-WO₃, was discovered. The electrochromic properties of Au-WO₃ proved to be quite different from those of the parent material, WO₃. This stage of the research program is summarized in Interim Annual Reports given in Appendix I. The details of the research prior to 1977 are described in the publications which are in Appendix II. The research undertaken in the final year (January 1977 to December 1977) is summarized below.

B. OPTICAL CONSTANTS OF COMPOSITE MATERIALS

The optical properties of the cermets Au-MgO and W-MgO and the composite semiconductors Si-CaF₂ and Si-MgO were studied in greater detail. The values of the optical constants of W-MgO were in agreement with the values derived from the Maxwell-Garnett equation with one exception: the major interband absorption peak was very much suppressed in the actual samples. This could be due to the very small grain sizes in the cermets. On the other hand, the measured optical constants of the Au-MgO were not only in disagreement with the Maxwell-Garnett theory but were also quite different from the constants of other Au cermets. Scanning-electron microscopy showed the surface of the Au-MgO to be textured on a scale of about 2000 Å. It is possible, though not yet established, that the observed values of the optical constants were influenced by increased absorption due to the texturing. The behavior of the composite semiconductors was largely in agreement with theory except for the appearance of a large absorption peak near 12 μm. It is possible that this anomalous absorption is due to chemical reactions between the constituents.

C. COMPARISON OF MAXWELL-GARNETT AND EFFECTIVE MEDIUM THEORIES

A comparison was made between the competing theories: Maxwell-Garnett theory and the effective-medium theory. It was concluded that the Maxwell-Garnett theory provides a good approximation to the complex dielectric constant of granular metals (cermets) while the effective-medium theory does not apply. Work addressed to this problem is being continued beyond the termination of the contract. A computer program, used at this laboratory primarily for solving electron optics problems, is capable, in principle, of computing the dielectric constant of a simulated composite formed by dispersing metallic (or dielectric) cylinders at random in an insulating matrix. However, for a large number of cylinders the computation time is prohibitively long and the expense correspondingly high. The question then arises: can this program be utilized in a practical way to calculate the optical constants of composite materials? As a first step the dielectric constant of a square array of metal cylinders was computed. Maxwell-Garnett computations agreed to a very high precision if the volume fraction of metal was less than 60%. Above 60% the agreement becomes progressively worse. This is expected since the dielectric constant must be singular at a volume fraction of $\pi/4$ when the cylinders touch one another; whereas no such singularity is predicted by Maxwell-Garnett. The effective-medium theory is in poor agreement with the calculations.

D. ELECTROCHROMIC CERMEITS

We have found that the electrochromism in the cermet Au-WO_3 is dominated by the pronounced absorption peak in the optical spectrum characteristic of most gold cermets.* Pure WO_3 is transparent in the visible and near infrared and is electrically insulating. When hydrogen is injected to form the solid solution H_xWO_3 , the material becomes conducting (metallic if x is sufficiently large) and colored a deep blue as a result of a broad absorption (peaked near $1 \mu\text{m}$) in the red and infrared. Before hydrogen injection, Au-WO_3 appears blue

* In this discussion we consider only those cermets in which the Au concentration is sufficiently small to preclude continuous conducting paths spanning the specimen.

as a result of a strong absorption peak at 6000 \AA . This absorption is characteristic of gold dispersions in dielectrics. Because SiO_2 has a smaller index of refraction than that of WO_3 the absorption in Au-SiO_2 is peaked near 5400 \AA , and the Au-SiO_2 cermet appears pink. This is understood in terms of the Maxwell-Garnett theory. Upon hydrogen injection, Au-WO_3 turns the deep-blue characteristic of WO_3 but within minutes "ripens" to a pink or rose color. The pink color is again a result of the absorption characteristic of Au cermet. The colored Au-WO_3 appears pink because the absorption has shifted from 6000 \AA prior to H-injection to 5500 \AA after injection. Further, the broad red-infrared absorption characteristic of colored WO_3 is missing in the "ripened" Au-WO_3 .

Like other sputtered cermet, as prepared Au-WO_3 is an insulator (at $T = 0 \text{ K}$) whose conductivity varies as $\exp(-aT^{-1/2})$. This temperature dependence is due to electron tunneling between Au grains. After H-injection, its conductivity is slightly increased and still varies as $\exp(-aT^{-1/2})$. This is to be contrasted with the pure WO_3 which can become metallic when colored. It should be noted that the lack of electrical conduction is related to the absence of the red-infrared absorption. In pure WO_3 the absorption band and the conductivity are associated with the hopping of electrons, which were donated by injected hydrogen, between W^{5+} and W^{6+} sites.

The reasons for the absence of conductivity and the absorption band are not yet known. However, if they are due to the absence of W^{5+} sites in the WO_3 matrix, the magnetic susceptibility of colored WO_3 and colored Au-WO_3 must be quite different, particularly at low temperatures. A study of the susceptibility of WO_3 and Au-WO_3 has been initiated. However, at the time of this writing there have been insufficient results to permit any conclusions to be drawn.

Appendix III contains the first draft of a paper detailing our study of the optical and electrical transport properties of the Au-WO_3 cermet.

II. PUBLICATIONS (January 1977 - December 1977)

1. J. I. Gittleman and B. Abeles, "Comparison of the Effective Medium and the Maxwell-Garnett Predictions for the Dielectric Constant of Granular Metals," Phys. Rev. B15, 3273 (1977).
2. E. K. Sichel, J. I. Gittleman, and J. Zelez, "Electrochromism in the Composite Material Au-WO₃," App. Phys. Lett. 31, 109 (1977).
3. J. I. Gittleman, B. Abeles, P. Zanzucchi, and Y. Arie, "Optical Properties and Selective Solar Absorption of Composite Material Films," Thin Solid Films 45, 9 (1977).

III. LIST OF PERSONNEL

During the period January 1977 to December 1977 the following Members of Technical Staff participated in the research: J. I. Gittleman (principal investigator), B. Abeles, E. K. Sichel, P. J. Zanzucchi, and R. W. Cohen.

IV. COUPLINGS (January 1977 - December 1977)

1. Solid State Seminar: B. Abeles, "Optical Properties of Composite Materials," Dept. of Physics, University of Arizona, Tucson, AZ, January 1977.
2. Invited Paper: J. I. Gittleman, "Optical Properties and Selective Solar Absorption of Composite Material Films," Int. Conf. Metallurgical Coatings, San Francisco, CA, March 28-April 1, 1977.
3. Solid State Seminar: B. Abeles, "Optical Properties of Composite Materials," Dept. of Physics, University of Puerto Rico, San Juan, Puerto Rico, March 1977.
4. Solid State Seminar: E. K. Sichel, "Electrochromism in the Composite Material Au-WO₃," Dept. of Physics, University of Cincinnati, Cincinnati, OH, June 1, 1977.

5. Submitted Paper: E. K. Sichel, "Electrochromism in the Composite Materials Au-WO₃," Electronic Materials Conf., Cornell University, Ithaca, NY, June 29-July 1, 1977.
6. Invited Talk: E. K. Sichel, "Electrochromism in the Composite Material Au-WO₃," Exxon Research and Engineering Co., Linden, NJ, June 21, 1977.
7. Invited Paper: B. Abeles, "Optical Properties of Composite Materials," Conf. Electrical Transport and Optical Properties of Inhomogeneous Media, Ohio State University, Columbus, OH, September 7-9, 1977.

APPENDIX I

Interim Reports for January 1 through December 31, 1975 and 1976

6

OPTICAL GRANULAR MATERIALS

J. I. Gittleman
RCA Laboratories
Princeton, New Jersey 08540

INTERIM ANNUAL REPORT
For the period 1 January 1976 to 31 December 1976

February 1977

Prepared for
Air Force Office of Scientific Research
Bolling Air Force Base
Washington, DC 20332

7

I. WORK STATEMENT

We propose to carry out a research program consisting of the synthesis of new granular materials, determination of their microstructures, and the determination of their optical and transport properties. Our efforts will be concentrated on the following activities:

- a. Synthesize granular systems using co-sputtering techniques to provide specimens having a wide range of composition.
- b. Form granular materials from suitable combinations of
 - (1) Metals with insulators such as Au, Ag, Mg, Al and W with SiO_2 , Al_2O_3 and WO_3 , and
 - (2) Semiconductors such as Ge and Si with insulators.
- c. Determine microstructure of specimens using electron micrography, electron and x-ray diffraction.
- d. Determine particle size and crystal structure as a function of time and temperature in a series of annealing studies.
- e. Observe the effect of annealing (item d) on the dielectric anomaly in granular metals, and correlate results with grain size.
- f. Determine the modulation spectrum of granular metals using piezoreflectance, and compare results with the known spectra of the parent elements.
- g. Determine the modulation spectra of granular semiconductors using electoreflectance, and compare results with the known spectra of the component materials.
- h. Measure the wavelength dependence of the optical density of films of co-sputtered metal- WO_3 composites as a function of electric field and metal concentration.

II. SUMMARY

During the past year the optical properties of the following composites were studied: Si-CaF_2 , Au-MgO , and Au-WO_3 . The first two were studied because of their potential use as selective absorbers of radiation or as filters. The latter material was chosen to obtain an understanding of its electrochromic behavior.

Measurements of (n,k) , the index of refraction and extinction coefficient for Si-CaF₂ composites were found to be in agreement with those computed from the Maxwell-Garnett theory using the optical constants of Si and CaF₂. The unannealed films exhibited a broad absorption edge which extended into the infrared. On annealing at 550°C, the absorption edge sharpened considerably. This result is consistent with Si grains being amorphous as prepared and becoming crystalline when annealed. In the far infrared, in addition to the CaF₂ Reststrahlen band near 40 μ m, an unexpected absorption was observed between 11 and 12 μ m. The most likely source of this absorption is the formation of a small amount of CaSiF₆. Thus, under our sputtering conditions, Si and CaF₂ do not form a completely immiscible system.

The optical properties of MgO-rich Au-MgO composites are not in agreement with Maxwell-Garnett theory. Although the transmittance exhibits a dielectric anomaly at the predicted wavelengths, the absorption is much less pronounced than predicted and the optical density remains larger than predicted, well into the infrared. Agreement with theory can be improved by adjusting the Drude part of the dielectric constant of the metal grains using electronic scattering times of $1-5 \times 10^{-16}$ s. However, the physical significance of such short times is obscure. Electron microscopy shows that although a number of the gold grains have diameters measuring 20 to 50 Å, a large fraction of the metal must be present as single atoms or clusters of a few atoms. Very little change (~ 1 k) in (n,k) was observed when specimens were annealed at 400°C. This suggests negligible growth of the Au grains.

Au-WO₃ is a new material: an electrochromic cermet. The coloration of WO₃ arises from the increase of absorption in the red and infrared accompanying an increase in conductivity. On the other hand, the color change in the cermet is dominated by shift in the wavelength at which the dielectric anomaly (characteristic of Au cermets) occurs. This shift is correlated with a change in the dielectric constant of the WO₃ matrix.

III. PUBLICATIONS

1. J. I. Gittleman, "Application of Granular Semiconductors to Photothermal Conversion of Solar Energy," Appl. Phys. Letters 28, 370 (1976).
2. B. Abeles and J. I. Gittleman, "Composite Material Films: Optical Properties and Applications," Applied Optics 15, 2328 (1976).

IV. LIST OF PERSONNEL

During this report period the following members of the Technical Staff participated in the research: J. I. Gittleman (Principal Investigator), B. Abeles, E. K. Sichel, H. W. Weakliem, Jr., P. J. Zanzucchi, and R. W. Cohen.

V. COUPLING

The following invited papers were presented by B. Abeles:

1. "Composite Material Films: Optical Properties and Applications," Optical Society Meeting on Optical Interference Coatings, Monterey, CA, Feb. 24-26, 1976.
2. "Electrical and Optical Properties of Composite Material Films," Physics Seminar, Ohio State University, Columbus, OH, Oct. 26, 1976.
3. "Physical Properties of Granular Metals," Division of Solid State Science Seminar, Argonne National Laboratory, Argonne, IL, Nov. 19, 1976.

VI. LIST OF PATENTS AND DISCLOSURES

The following disclosures were made during the past year:

1. "Electrochromic Behavior of Cermet Films" RCA Docket #71,156, E. K. Sichel.
2. "Improved Electrochromic Material" RCA Docket #71,343, E. K. Sichel.

OPTICAL GRANULAR MATERIALS

J. I. Gittleman
RCA Laboratories
Princeton, New Jersey 08540

INTERIM ANNUAL REPORT
For the period 1 January 1975 to 31 December 1975

February 1976

Prepared for
Air Force Office of Scientific Research
Bolling Air Force Base
Washington, DC 20332

I. WORK STATEMENT

The contractor shall furnish scientific effort during the contract period together with all related services, facilities, supplies, and materials needed to conduct the following research:

- a. Synthesize granular systems using co-sputtering techniques to provide specimens having a wide range of composition.
- b. Form granular materials from suitable combinations of:
 - (1) Metals with insulators and semiconductors,
 - (2) Semiconductors such as germanium and silicon with insulators,
 - (3) Semimetals such as bismuth or degenerate SnO_2 with insulators.
- c. Determine microstructure of specimens using electron micrography, electron and x-ray diffraction.
- d. Determine particle size and crystal structure as a function of time and temperature in a series of annealing studies.
- e. Determine the optical properties of these materials in the visible and infrared, using reflectivity and transmissivity measurements in the wavelength range from about $0.3 \mu\text{m}$ to as far as $150 \mu\text{m}$.
- f. Determine electrical transport properties of these materials as a function of temperature.
- g. Compare experimental results with existing theories.
- h. Develop new theories where existing theories are inadequate.

II. SUMMARY

During the past year, films of finely divided composites were made from the immiscible systems Ag-SiO_2 , $\text{Ge-Al}_2\text{O}_3$, and SiC-Si , using co-sputtering techniques. The results of the research on these systems are summarized below.

A. Ag-SiO_2 . - For the first time surface plasmons were observed in a granular metal. Plasma resonance absorption measurements were used to determine the plasma frequency over the entire compositional range. The observed decrease of the plasma frequency with increasing insulator concentration is in quantitative agreement with the Maxwell-Garnett theory.

B. $\text{Ge-Al}_2\text{O}_3$. - Films of granular germanium with concentrations below 50 vol % were sputtered onto aluminum mirrors. Reflectivity measurements for wavelengths below $5 \mu\text{m}$ were in good quantitative agreement with the Maxwell-Garnett theory. Calculations demonstrate that granular germanium and silicon sputtered on

reflecting surfaces are expected to provide highly selective absorbers for the photothermal conversion of solar energy.

C. SiC-Si. - The granular SiC-Si system was chosen for study for two reasons: (1) It is well known to be immiscible for all compositions so that the complications of alloy-formation and chemical reaction are avoided, and (2) SiC exhibits a simple *Reststrahlen* absorption anomaly at a wavelength (12.6 μm) where silicon is highly transparent. Thus, this system is among the simplest for studying the lattice absorption of finely divided grains. The research on this system is not yet complete. Below we summarize the results to date.

Sputtered films of pure SiC were amorphous, with some grain growth observed after annealing at high temperatures (1000°C for 2 h in argon). The optical properties at wavelengths both near the energy gap and near the lattice absorption were in excellent agreement with published results. Films of SiC-Si also were amorphous as sputtered, and electron diffraction showed some grain growth after annealing at 1000°C. Film composition was readily determined using electron microprobe techniques. For the amorphous films, the lattice absorption (12.6 μm for pure SiC) was observed to shift to longer wavelengths as the silicon concentration was increased. For the annealed films, the lattice absorption shifted to shorter wavelengths, in quantitative agreement with the Maxwell-Garnett theory.

D. Theoretical Considerations. - Recent articles have suggested that the so-called "selfconsistent effective medium theory" better describes the optical properties of composite systems than does the Maxwell-Garnett theory. However, our calculations show that this theory is incapable of predicting the observed shift in either the plasma frequency or the frequency of the absorption anomaly in either metal-insulator systems or in the SiC-Si system, whereas the Maxwell-Garnett theory has been shown to predict these shifts quite accurately.

III. PUBLICATIONS

1. E. B. Priestley, B. Abeles and R. W. Cohen, "Surface Plasmons in Granular Ag-SiO₂ Films," *Phys. Rev. B*, **12**, 2121 (1975).
2. J. I. Gittleman, "Application of Granular Semiconductors to Photothermal Conversion of Solar Energy," *Appl. Phys. Letters*, to be published, April 1, 1976.

IV. LIST OF PERSONNEL

During this report period the following members of the Technical Staff participated in the research: J. I. Gittleman (Principal Investigator), B. Abeles, H. A. Weakliem, Jr., P. J. Zanzucchi, E. B. Priestley, and R. W. Cohen.

V. COUPLING

An invited paper entitled "Optical Properties of Films of Composite Materials" was presented by B. Abeles at the Symposium on The Fundamental Optical Properties of Solids Relevant to Solar Energy Conversion, Nov. 20-23, 1975, at Tuscon, Arizona. The symposium was sponsored by NSF.

VI. LIST OF PATENTS AND DISCLOSURES

No patents, applications, or disclosures were submitted during the report period.

APPENDIX II

Publications (Reprints)

RCA

Surface Plasmons in Granular Ag-SiO₂ Films

E. B. Priestley, B. Abeles, and R. W. Cohen

Reprinted from Physical Review B, Vol.12, No.6, 15 September 1975

RCA LABORATORIES PRINCETON, NEW JERSEY



DAVID SARNOFF RESEARCH CENTER

Surface plasmons in granular Ag-SiO₂ films*

E. B. Priestley, B. Abeles, and R. W. Cohen

RCA Laboratories, Princeton, New Jersey 08540

(Received 29 January 1975)

We report the first observation of surface plasmons in a granular metal. The plasma frequency ω_p in the Ag-SiO₂ system is determined from plasma resonance absorption measurements over the entire range of composition from the continuous-metal-film limit to the isolated-metal-particle limit. The observed decrease in ω_p with increasing insulator concentration is understood within the framework of the phenomenological Maxwell-Garnett theory.

Surface plasmons¹ have been studied extensively both in continuous-metal films²⁻⁸ and in isolated-metal particles.⁹⁻¹³ However, there have been no reported experimental studies of surface plasmons in particulate systems for which the isolated-particle approximation breaks down. Granular metals¹⁴ are ideal materials in which to study surface-plasmon behavior, because the interparticle distance can be varied by varying the volume fraction x of the insulator component. When x is small the metal grains coalesce, forming a metallic continuum with dielectric inclusions. In the limit $x \rightarrow 1$, the inverse structure is obtained with isolated crystalline metal grains dispersed in a dielectric matrix. A transition between these structures occurs in the intermediate range of composition.

In this paper we report the first observation of surface plasmons in a granular metal. We have studied the Ag-SiO₂ system for $0 \leq x \leq 0.85$ using the plasma resonance absorption technique.⁸ This is the first material for which the evolution of the plasma frequency has been followed from the continuous-metal-film limit to the isolated-metal-particle limit. Our results agree well with the predictions of the Maxwell-Garnett theory.

Granular Ag-SiO₂ films were prepared as described in Refs. 15 and 16. The weight fractions of Ag and SiO₂ (determined spectroscopically) together with the measured film density, were used to determine the volume fraction x of insulator in the granular metal to an accuracy of $\pm 5\%$. While the densities of the sputtered silver and SiO₂ films were found to be equal to those of the bulk materials (within an experimental uncertainty of $\pm 3\%$), the densities of the granular metals were substantially lower than would be expected from a void-free composite of silver and vitreous silica. In view of the extreme immiscibility of Ag and SiO₂, it is likely that the silica does not completely fill the space between the Ag particles, and the resulting voids are responsible for the observed density depression. We concluded that the silver in our Ag-SiO₂ samples did have the bulk density since electron diffraction and electron microscopy showed

it to be in the form of crystalline grains with a lattice constant equal to that of bulk silver. The voids produce an average insulator density S_i lower than that of bulk SiO₂. When plotted against total volume fraction x of insulator, the void concentration is a bell shaped function which is zero at $x=0, 1$ and which reaches a maximum near $x=0.5$ (the composition at this point, expressed as volume fractions, is 0.5 Ag, 0.3 SiO₂, and 0.2 voids).

Transmission electron micrographs, shown in Fig. 1, were obtained from 300-Å-thick films sputtered onto carbon film substrates supported by a fine copper mesh. Coalescence of the silver particles due to heating by the microscope electron beam¹⁵ was suppressed by overcoating the granular metal films with a thin layer of carbon.

Polarized absorption measurements were made in the wavelength range 3000–5000 Å on 400-Å-thick films supported by quartz substrates. The samples were oriented so the incident light impinged at an angle of 60° to the film normal. Measured spectra for films with $x=0.08$ and 0.61 are shown in Fig. 2. The p -polarized wave is absorbed at a wavelength corresponding to the plasma frequency, whereas the s -polarized wave does not couple to the surface plasmon and no absorption is observed. In metal-rich films (small x) the absorption peak was well resolved [Fig. 2(a)]. However, in the dilute limit the absorption was quite small [Fig. 2(b)] and identification of a peak in the p -polarized spectrum was difficult. Since the s -polarized wave does not excite plasmons, the spectrum observed with this polarization of light represents a background absorption level in the vicinity of the plasma resonance peak. Therefore, the s -polarized spectrum was subtracted from the p -polarized spectrum to enhance the absorption peak.

We have analyzed our results in terms of the phenomenological Maxwell-Garnett theory, generalized to include nonspherical particles.¹⁵ The theory takes into account the modification of the incident electromagnetic \vec{E} field by the dipole fields of the individual polarizable silver grains and provides a relationship between the frequency depen-

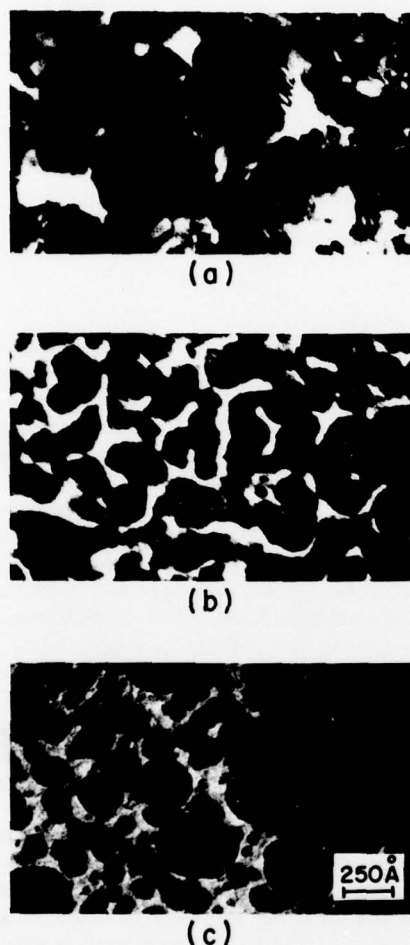


FIG. 1. Electron micrographs of three representative samples having different volume fraction x of insulator: (a) $x=0.25$, (b) $x=0.5$, and (c) $x=0.7$.

dent dielectric constant $\epsilon(\omega)$ of the composite material and the dielectric constants $\epsilon_m(\omega)$ and $\epsilon_i(\omega)$ of its metal and insulator constituents, namely,

$$\frac{\epsilon(\omega) - \epsilon_i(\omega)}{L_m \epsilon_m(\omega) + (1 - L_m) \epsilon_i(\omega)} = (1 - x) \times \frac{\epsilon_m(\omega) - \epsilon_i(\omega)}{L_m \epsilon_m(\omega) + (1 - L_m) \epsilon_i(\omega)}, \quad (1)$$

where L_m is the depolarization factor corresponding to the shape of the metal particles. Equation (1) is not valid in the metal-rich limit since the material then consists of dielectric inclusions in a continuous metal matrix and the dielectric constant is properly described by inverting the roles of the metal and insulator components. This is accomplished by performing the transformation

$\epsilon_m \leftrightarrow \epsilon_i$, $(1 - x) \rightarrow x$, and $L_m \rightarrow L_i$ in Eq. (1).

The plasma frequency is defined as that frequency for which $\text{Re}[\epsilon(\omega)] = 0$.¹⁷ Substituting values¹⁸ for $\epsilon_i(\omega)$ in Eq. (1), we solved for the values of $\epsilon_m(\omega)$ that satisfied this condition, and subsequently determined ω_p using the dielectric constant data for bulk silver published by Ehrenreich and Philipp.¹⁹ Following Cohen *et al.*,¹⁵ we have also determined the dependence on x of λ_A , the wavelength for which $\epsilon_2(\omega)$ of the granular metal reaches a local maximum due to the singularity in the expression for the local field. Our experimental measurements of the dependence of $\lambda_p (= 2\pi c/\omega_p)$ and λ_A on x , together with the behavior predicted by Eq. (1) for spherical ($L_m = \frac{1}{3}$) and cylindrical ($L_m = \frac{1}{2}$) particles, are shown in Fig. 3.

For $x > 0.45$, a good fit to the data is obtained by treating L_m as an adjustable parameter with a value of 0.385, corresponding to prolate spheroids having an axial ratio of ~ 1.2 . This is consistent with the particle shapes observed in the electron micrographs [Fig. 1(c)]. However, the value of L_m for nonspherical particles depends upon their orientation relative of the \vec{E} vector of the excited mode. Since our samples are composed of randomly oriented particles (Fig. 1), it is not strictly meaningful to characterize a sample by a single depolarization factor. It is interesting, nonetheless, that the data can be fit rather well over a large range of composition with a single parameter

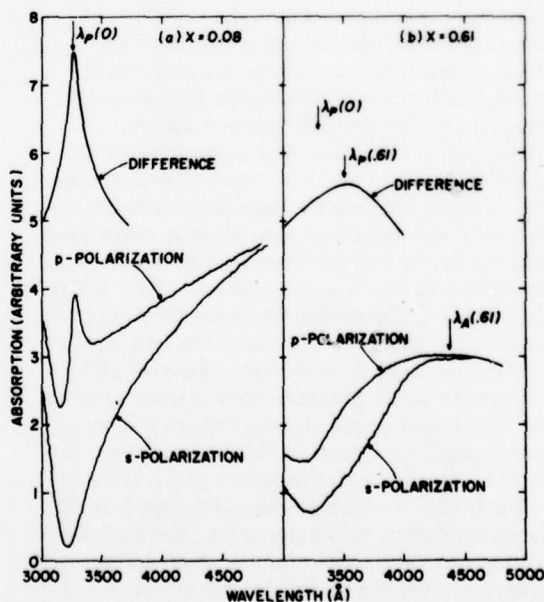


FIG. 2. Absorption spectra for the two polarizations of incident light: (a) $x=0.08$ volume fraction and (b) $x=0.61$ volume fraction insulator. Also shown is the difference between the s - and p -polarized spectra.

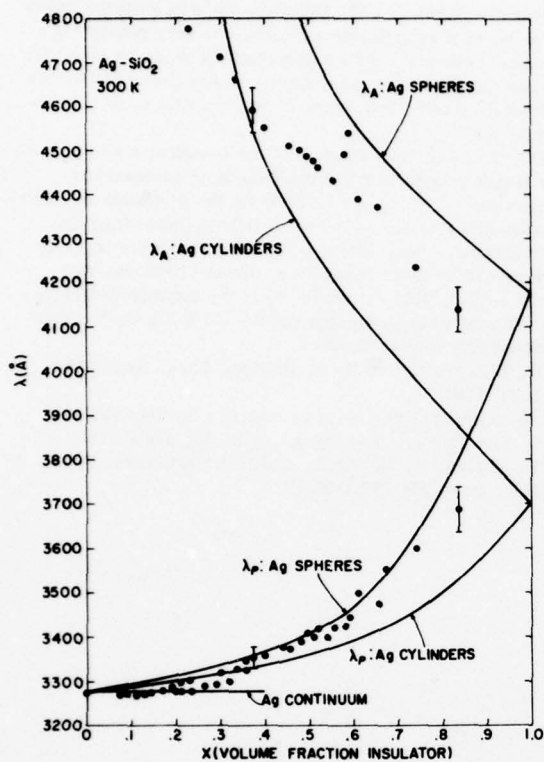


FIG. 3. Plot of the experimental data points for λ_p and λ_A as a function of volume fraction insulator. Also included are curves calculated using a generalized Maxwell-Garnett theory for spherical and cylindrical silver particles.

L_m . As x is reduced below 0.6 the Ag particles begin to coalesce and their shapes become complex [Fig. 1(b)]. This structural transition is manifested in the optical measurements as a gradual change from near-spherical to near-cylindrical particles (the change is not as evident in the λ_p data as it is in the λ_A data because the effect of particle shape on λ_p is smaller than it is on λ_A). In contrast to this gradual change in the optical properties, the dc electrical resistivity (Fig. 4) indicates an abrupt transition from nonmetallic to metallic behavior near $x = 0.6$. This difference is not unreasonable if one considers the physical processes involved. At the percolation threshold^{16,20,21}

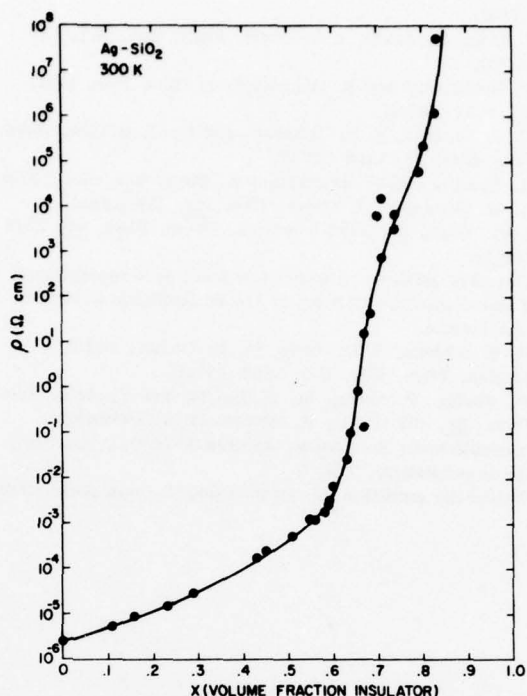


FIG. 4. Plot of the measured resistivities as a function of volume fraction insulator.

it takes very few conductive channels to produce the observed abrupt change in resistivity. Thus, the electrical transition occurs at concentrations for which the Ag particles have just begun to coalesce. On the other hand, it requires a much greater degree of coalescence to alter the optical behavior appreciably, and the optical transition occurs for smaller values of x and over a broader range. In the very metal rich samples [$x \leq 0.2$, Fig. 1(a)], the observed plasma frequency is independent of composition, in agreement with the theory when the roles of the metal and insulator are inverted.¹⁵

We wish to thank H. H. Whitaker for the chemical analyses, and M. D. Coutts for the electron micrographs. We are grateful to G. D. Cody and J. I. Gittleman for helpful suggestions and to Y. Arie and J. F. McLaughlin for their competent technical assistance.

*Research supported in part by the Air Force Office of Scientific Research (AFSC) under Contract No. F44620-75-C-0057.

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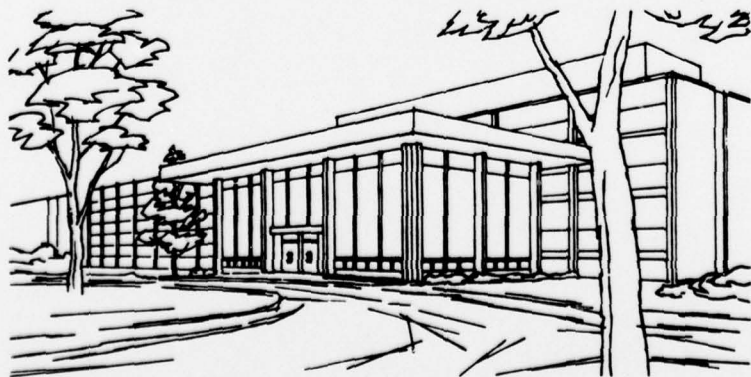


Application of Granular Semiconductors to Photothermal Conversion of Solar Energy

J. I. Gittleman

Reprinted from Applied Physics Letters, Vol.28, No.7, 1 April 1976

RCA LABORATORIES PRINCETON, NEW JERSEY



DAVID SARNOFF RESEARCH CENTER

Application of granular semiconductors to photothermal conversion of solar energy*

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(Received 20 November 1975)

A novel selective solar absorber, consisting of a dispersion of semiconductor grains in a low-dielectric-constant insulator is proposed. Calculations based on Maxwell-Garnett theory show that because of its lower reflectivity for $\lambda < 1.5 \mu\text{m}$ this material is about 60% more efficient than silicon in converting solar energy to heat. Reflectivity measurements for Ge-Al₂O₃ films on aluminum agree with the predictions of the Maxwell-Garnett theory. The problems associated with the reduction to practice are discussed.

PACS numbers: 84.60.Rb, 78.65.+t, 81.60.+k

There has been a developing interest in absorbers for photothermal conversion of solar energy, particularly absorbers capable of operating efficiently at temperatures appropriate for steam power plant operations.¹ An absorber that has been considered is a layer of silicon on a highly reflecting surface.² For wavelengths greater than $1.0 \mu\text{m}$ the silicon is transparent and the absorber has very low emissivity. For shorter wavelengths the silicon becomes absorbing. However, because of its large index of refraction n , a Si absorber loses much of the available solar energy by reflection. The use of antireflection coatings has been suggested² as a means of increasing the absorption. An alternative which may have economical advantages over multiple-layer designs is to replace the silicon layer by an appropriate granular semiconductor. A granular semiconductor film is formed by cosputtering a semiconductor and an insulator with which it is immiscible. Such a material is structurally similar to granular metals (dispersions of metal particles in insulators) for which

there exists a sizeable literature.³ Mixing a semiconductor with an insulator having a low refractive index would be expected to result in a granular semiconductor with an index smaller than that of its semiconductor component. Hence if the mixing does not reduce the extinction coefficient beyond a tolerable value, the absorbance of the granular semiconductor will be high and its reflectance will be low.

Studies by Cohen *et al.*⁴ have shown that the optical properties of granular metals are governed by the Maxwell-Garnett equation. For the case of spherical grains, this is given by

$$(\epsilon - \epsilon_a)/(\epsilon + 2\epsilon_a) = x(\epsilon_b - \epsilon_a)/(\epsilon_b + 2\epsilon_a), \quad (1)$$

TABLE I. Effect of increased absorbance of the Ge-Al₂O₃ on photothermal conversion.

	Incident solar energy ^a (W/m ²)	Solar energy converted to heat at 750 K ^b (W/m ²)	Relative performance (%)
Ideal ^c	956	775	100
Si ^d	956	380	49
Ge ^e	956	365	47
Ge-Al ₂ O ₃ ^f	956	605	78

^a Under conditions of 1 standard air mass and no concentration of radiation.

^b See Ref. 2 for a discussion of principles involved in determining net solar energy absorbed by a selective absorber.

^c Reflectance = 0 for $\lambda < 1.5 \mu\text{m}$ and 1 for $\lambda > 1.5 \mu\text{m}$ (for an absorber at 750 K).

^d Optical data from Ref. 5.

^e Optical data from Ref. 6.

^f Assuming 35 Vol. % of crystalline Ge and ignoring the lattice absorption of Al₂O₃.

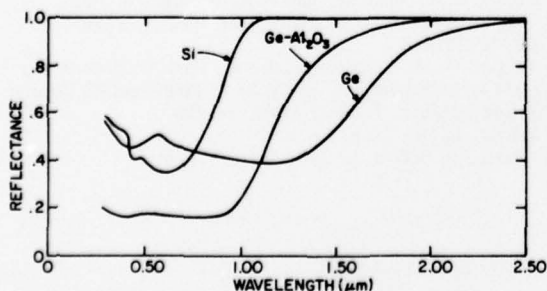


FIG. 1. Reflectance vs wavelength for 5- μm -thick films on perfect mirrors (interference averaged).

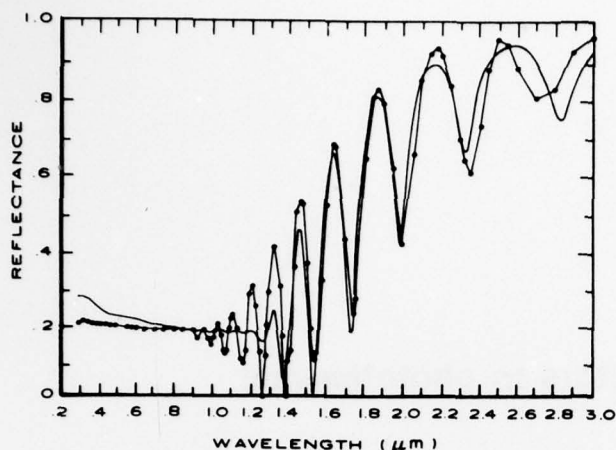


FIG. 2. Reflectance of a 2.8- μm -thick film of $\alpha\text{-Ge-Al}_2\text{O}_3$ containing 35 Vol. % Ge deposited on Al. Continuous curve computed from Eq. (1); experimental points are connected by straight lines.

where x is the volume fraction occupied by the metal particles, ϵ_a is the dielectric constant of the insulating matrix, ϵ_s is the dielectric constant of the metal, and ϵ is the dielectric constant of the granular metal. Assuming Eq. (1) to be applicable, the improvement of the granular semiconductor over the bulk semiconductor is dramatic. Figure 1 shows the reflectance vs wavelength computed for 5- μm films of Si, Ge, and granular $\text{Ge-Al}_2\text{O}_3$ containing 30 Vol. % Ge deposited on perfect mirrors. The effect of the increased absorbance of the $\text{Ge-Al}_2\text{O}_3$ on photothermal conversion is illustrated in Table I. It can be seen that the granular Ge converts about 60% more energy than does Si. This is due, in part, to its smaller reflectance at short wavelengths and in part due to its smaller energy gap, which permits absorption to longer wavelengths.

To check the applicability of Eq. (1), layers of $\text{Ge-Al}_2\text{O}_3$ on Al films were prepared using cosputtering techniques reported elsewhere.⁷ X-ray diffraction studies of $\text{Ge-Al}_2\text{O}_3$ films indicated that both the Ge and the Al_2O_3 were amorphous. Using published values of the optical constants of $\alpha\text{-Ge}$ ⁸ and Al_2O_3 ,⁹ the optical constants of $\text{Ge-Al}_2\text{O}_3$ were computed from Eq. (1). These results, along with the measured reflectance of the Al films, were used to compute the reflectance of our specimens. Typical results for a specimen containing 35 Vol. % Ge are shown in Fig. 2 along with experimental points (which are joined by straight lines). Agreement is excellent except near 1 μm where the measured amplitudes of the interference fringes differ from the theoretical values. Such deviations are not unexpected since the optical constants of $\alpha\text{-Ge}$ depend somewhat on the method of preparation.^{8,10}

Although theory indicates that granular semiconductors have the potential to provide very efficient photothermal conversion, some important materials problems must be solved before that potential can be realized. The first is the choice of the semiconductor component. Using the optical constants determined at room temperature, granular Ge is superior to granular Si. However, the reduction of the energy gap at high temperatures favors increased efficiency for Si and decreased efficiency for Ge. Further, the extended "tail" of the absorption edge in amorphous semiconductors makes crystallinity in the semiconducting component essential. This could be accomplished by annealing or depositing on hot substrates. Finally, an insulator must be found which (i) does not react with the semiconductor, (ii) is essentially transparent to at least 20 μm , and (iii) can withstand operating temperatures of 750 K or more.

We have shown that granular semiconductors are a class of materials which are potentially capable of efficient absorption of solar energy. In fact converter performance approaching the ideal (see Table I) can be obtained provided the above materials problems are solved.

The author would like to thank B. Abeles and Y. Arie for providing the specimens, P.J. Zanzucchi and D.A. Kramer for the reflectance measurements, and R.W. Cohen for helpful discussions.

*Research supported in part by Air Force Office of Scientific Research (AFSC) under Contract No. B44620-75-O-0057.

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RCA

Composite material films: optical properties and applications

B. Abeles and J. I. Gittleman

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DAVID SARNOFF RESEARCH CENTER

Composite material films: optical properties and applications

B. Abeles and J. I. Gittleman

The optical properties of the composite systems Ag-SiO₂, Si-SiC, and Ge-Al₂O₃ are compared with the predictions of the Maxwell-Garnett and the effective medium theories. Only the Maxwell-Garnett theory predicts the characteristic optical features of granular metals—a red shift relative to the pure metal in the plasma resonance and a dielectric anomaly. In the case of Si-SiC, the observed red shift in the transverse optical phonon frequency is too small to allow one to discriminate between the two theories. In the case of the Ge-Al₂O₃ films, both theories are in good agreement with the experimental results for the optical constants near the absorption edge. The use of composite films for photothermal conversion and other optical applications is discussed.

I. Introduction

The composite materials discussed in this paper are multiphase systems consisting of mixtures of immiscible metals and insulators¹ and of semiconductors and insulators.² The metal mixtures are commonly referred to as granular metals (or cermets) and the semiconductor mixtures as granular semiconductors. The microstructure of these materials depends on the volume fractions of the components. This is illustrated in Fig. 1 by the electron micrographs of sputtered granular Au-Al₂O₃ films.¹ In the metallic region, where the volume fraction of the metal is large [Fig. 1(a)], the metal grains touch and form a continuum with dielectric inclusions. In the dielectric region [Figs. 1(c) and 1(d)] the structure is inverted, the metal grains are isolated, and the insulator forms the continuum. In the transition region where the structural inversion takes place between the metallic and dielectric regions, the metal and insulator form a labyrinth structure [Fig. 1(b)]. A similar dependence of structure on composition is expected in the case of granular semiconductors.

Granular metals and granular semiconductors represent interesting systems in which to study the optical properties of randomly inhomogeneous mixtures. One of the objectives of such studies is to learn how to predict the optical constants of the system, given those of the components. The theory that has so far been proved to be the most successful one is the Maxwell-Garnett theory (Sec. II). The optical phenomena that are discussed in this paper are the shift in the plasma frequency³⁻⁵ and the appearance of a dielectric anomaly

in granular metals³⁻⁷ (Sec. III), the lattice absorption of SiC in granular SiC-Si films, and the absorption edge of Ge in Ge-Al₂O₃ films² (Sec. IV). Some of the applications of optical composite materials are discussed in Sec. V.

II. Theory

The optical properties of random inhomogeneous materials are of general interest because of the wide variety of systems in which they occur. Such systems are described by a spatially varying dielectric constant $\epsilon(\mathbf{r}, \omega)$, where \mathbf{r} is the coordinate vector and ω the frequency. When the wavelength of light is much larger than the spatial variation of $\epsilon(\mathbf{r}, \omega)$, the systems can be characterized by a well-behaved complex dielectric constant $\epsilon_S(\omega)$. The calculation of $\epsilon_S(\omega)$ from $\epsilon(\mathbf{r}, \omega)$ is a forbidding mathematical problem, and approximate solutions must be sought for special cases.⁸

The composite materials described in this paper are binary mixtures. The grains of the two phases are assumed to be much smaller than the wavelength of light, but they are large enough so that they can be characterized by macroscopic dielectric constants. Approximate solutions to the integral equation from which ϵ_S is determined are obtained by neglecting multiple scattering of the electric field by the grains.⁸ This approximation is equivalent to a mean field theory in which the effect of all the grains on a given grain is represented by a uniform field. Two well-known approximations are the effective medium theory⁹ and the Maxwell-Garnett theory.¹⁰

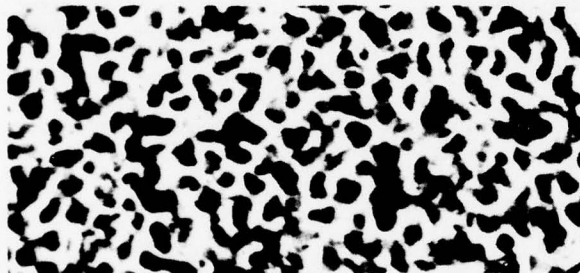
In the effective medium theory the two components, A and B, are treated in an equivalent manner. Grains of A and B are embedded in an effective medium whose dielectric constant is ϵ_S , the same as that of the com-

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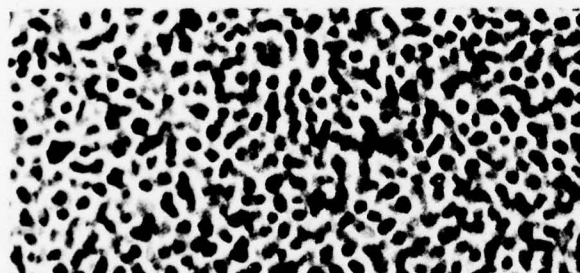
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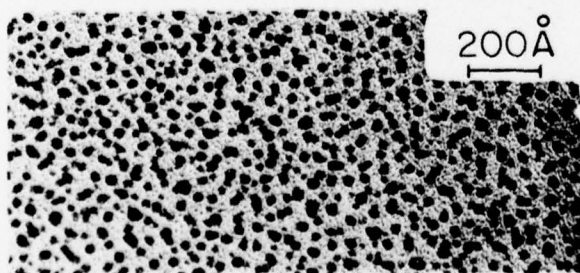
(a) 73 Vol. % Au



(b) 48 Vol. % Au



(c) 35 Vol. % Au



(d) 18 Vol. % Au

Fig. 1. Electron micrographs of sputtered Au-Al₂O₃ films. The vol% of Au and length scale are indicated in the figure. The thicknesses of the films are (a) 110 Å, (b) 140 Å, (c) 110 Å, and (d) 70 Å. (After Abeles *et al.*¹)

posite material. The choice of the effective medium is such that the average field acting on a grain due to all the other grains averages to zero. The dielectric constant ϵ_S , in the case where grains of A and B are spherical is given by the relation⁸:

$$x \frac{\epsilon_A - \epsilon_S}{\epsilon_A + 2\epsilon_S} + (1-x) \frac{\epsilon_B - \epsilon_S}{\epsilon_B + 2\epsilon_S} = 0, \quad (1)$$

where x is the volume fraction of component A, and ϵ_A and ϵ_B are the dielectric constants of the individual grains.

In the Maxwell-Garnett theory it is assumed that the grains of one component are embedded in the matrix of the other component. This theory, unlike the effective medium theory, treats the two components in an asymmetric manner. The field acting on a grain due to all the other grains is assumed to be given by the Lorentz local field. The expression for ϵ_S , generalized to the case for which the grains of A (embedded in matrix B) are rotational ellipsoids identical in shape and orientation (but not necessarily in size), is given by⁶:

$$\frac{\epsilon_S - \epsilon_B}{L\epsilon_S + (1-L)\epsilon_B} = x \frac{\epsilon_A - \epsilon_B}{L\epsilon_A + (1-L)\epsilon_B}, \quad (2)$$

where L is the characteristic depolarization factor. For spherical grains ($L = 1/3$), Eq. (2) reduces to the usual Maxwell-Garnett result.¹⁰

Inspection of Eqs. (1) and (2) shows that their forms are entirely different: Eq. (1) is quadratic in ϵ_S and symmetric in ϵ_A and ϵ_B , while Eq. (2) is linear in ϵ_S and asymmetric in ϵ_A and ϵ_B . Equation (2) is expected to be applicable in systems in which grains of one component are dispersed in the matrix of the other component (e.g., the metallic and dielectric regions of granular metals) and inapplicable in the transition region. The effective medium theory is expected to be applicable in systems in which the shapes of the grains of the two components are similar.

III. Granular Metals

The unusual optical properties of systems of small metal particles have been known for hundreds of years. Such systems exhibit a strong optical absorption peak that is absent in the bulk metal. An example of this is given by gold colloidal particles suspended in glass in which the absorption peak gives rise to a beautiful ruby-red color. The absorption peak in granular metals has been referred to as a dielectric anomaly⁶ because ϵ_S has the frequency dependence characteristic of a strongly damped dielectric anomaly. The dielectric anomaly in granular metals can be viewed as a displacement to optical frequencies of the dc anomaly of the pure metal.

The two granular metal systems that have been studied most widely are those using Au and Ag. The reason for this choice of metals is that the absorption peaks for these systems lie in the readily available optical 3000–5000-Å range. The absorption peaks have been observed in discontinuous metal films,^{10,11} on rough surfaces of metals,¹² in metal dispersions in glasses,^{10,13} and in cermets.^{3,6,14,15} In the case of the discontinuous films, there are difficulties in a quanti-

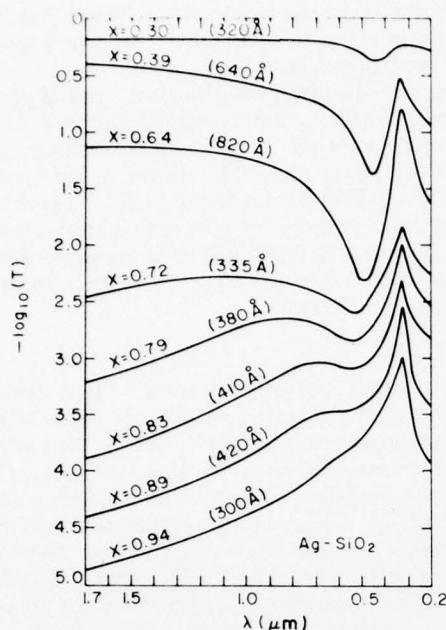


Fig. 2. Log of optical transmission T (measured at normal incidence) vs wavelength λ in sputtered Ag-SiO₂ films. The volume fractions x of Ag and the film thicknesses are indicated. (After Cohen *et al.*⁶)

tative interpretation of the data because of the ambiguities in film thickness, the insulator dielectric constant, and the volume fraction of metal.¹¹ In the case of three-dimensional granular metal systems, the film thickness and the dielectric constant of the insulator are well defined, and, unlike in discontinuous metal films, it is possible to vary the film thickness and the volume fraction of the metal independently. Such systems are therefore more appropriate for testing the validity of theories. The more recent measurement on three-dimensional granular metals include those on Ag and Au grains grown in photosensitive glasses¹³ and those on Ag-SiO₂ and Au-SiO₂ cermet systems.^{3,6}

In Fig. 2 are shown the optical transmission measurements made on sputtered Ag-SiO₂ films as a function of the wavelength of the light.⁶ The characteristic absorption peak in the visible is seen to develop as the volume fraction of Ag is decreased. At the same time the infrared behavior, characteristic of a metal (an increasing transmission with decreasing wavelength), is seen to change to one characteristic of an insulator (high transmission).

In Fig. 3 are compared the predictions of Eqs. (1) and (2) with the observed optical density for one of the films in Fig. 2.¹⁶ The theoretical curves were computed using for ϵ_A the dielectric constant of Ag,¹⁷ assuming spherical grains for the Ag, and for ϵ_B the dielectric constant of SiO₂ ($\epsilon_B = 2.2$). The Maxwell-Garnett theory [Eq. (2)] predicts reasonably well the position of the absorption peak, but the predicted height of the peak is larger than observed. On the other hand, the effective medium theory yields no distinctive absorption peak.

In Fig. 4 are plotted the wavelength corresponding

to the absorption peak λ_A and the plasma resonance wavelength λ_p (determined from transmission measurements at oblique incidence³) as a function of x . The plasma resonance frequency ω_p was calculated from the relation $\text{Real}[\epsilon_S(\omega_p)] = 0$.³ Equation (1) predicts no change of ω_p with composition. Equation (2) predicts a decrease of ω_p with x in the dielectric region; as $x \rightarrow 0$ (noninteracting Ag grains), $\omega_p \rightarrow \omega_A$; and an ω_p independent of x and equal to the bulk value in the metallic region. The experimental data are seen to fall between the curves corresponding to Eq. (2) for spheres and cylinders.

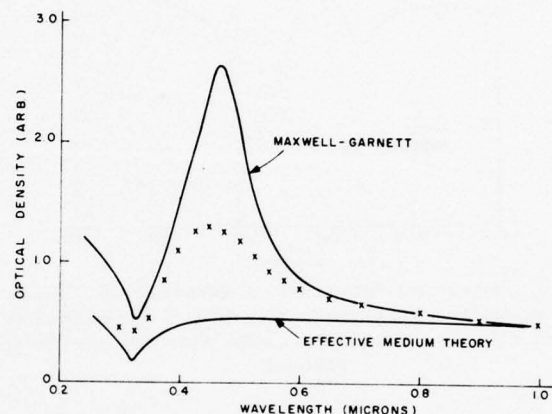


Fig. 3. Optical density of Ag-SiO₂ film containing 0.39 volume fraction Ag. Theoretical curves computed from Eqs. (1) and (2); experimental data points are represented by crosses. (After Gittleman and Abeles.¹⁶)

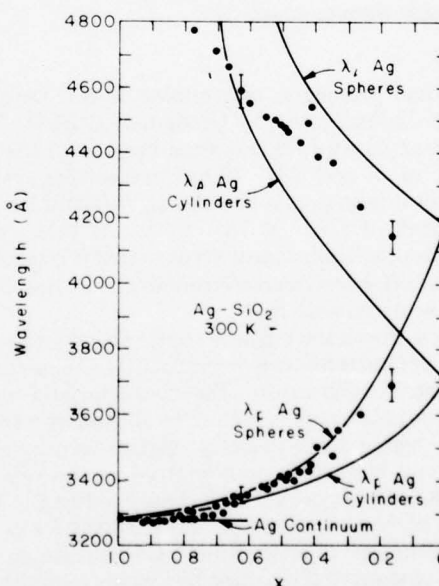


Fig. 4. Plot of the experimental data points for λ_p and λ_A as a function of volume fraction of insulator. Full curves calculated from Eq. (2) for spherical ($L = \frac{1}{2}$) and cylindrical ($L = \frac{1}{2}$) Ag grains using for ϵ_A the dielectric constant of bulk Ag and for ϵ_B the dielectric constant of the insulator. (After Priestley *et al.*³)

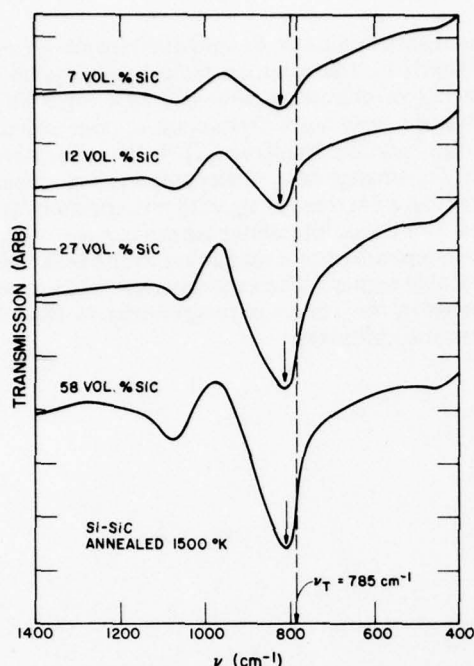


Fig. 5. Transmission characteristics of sputtered Si-SiC films on Si substrates for various volume fractions of SiC.¹⁹ The wavenumber corresponding to the transverse optical phonon in pure SiC is indicated.

The above results show conclusively that the effective medium theory is not applicable to granular metals. It should be noted though that the theory has been applied with some success to other random inhomogeneous systems.¹⁸

IV. Granular Semiconductors

A. Si-SiC

The optical properties of granular Si-SiC have recently been investigated by Gittleman *et al.*¹⁹ The authors chose to study this system because of the immiscibility of Si and SiC. What makes this system particularly interesting is the strong reststrahlen absorption peak of SiC²⁰ at 785 cm^{-1} . At that wavenumber Si is practically transparent so that it is possible to study the effect on the reststrahlen absorption peak when SiC is mixed with Si.

In Fig. 5 is shown the infrared transmission measured on a series of sputtered and subsequently annealed Si-SiC films on Si substrates. The characteristic reststrahlen absorption peak is seen to be shifted by a small amount to higher wavenumbers relative to pure SiC. The observed blue shift $\Delta\nu$ is plotted vs the volume fraction SiC and compared with theory in Fig. 6. The theoretical curve computed from Eq. (2) using for ϵ_A the dielectric constant of crystalline SiC²⁰ and for ϵ_B the dielectric constant of crystalline Si²¹ yields a small blue shift that increases linearly with the volume fraction of Si. A similar calculation based on Eq. (1) results in no shift of the absorption peak.

A large red shift of the absorption peak (shown in Fig.

6) was observed in the films prior to annealing. This red shift is believed to be due to the amorphous nature of the films prior to annealing.

The observed shift of the absorption peak in the annealed Si-SiC films is unfortunately too small to allow one to make definitive conclusions regarding the applicability of the theories. The reason for the frequency shift being so small is believed to be due in part to the fact that the dielectric constant of Si is so close to that of SiC. A larger frequency shift is expected if SiC is mixed with a material whose dielectric constant is substantially different.

B. Ge-Al₂O₃

The optical properties of granular Ge in the wavelength range near the absorption edge of Ge were reported by Gittleman.² Figure 7 shows the results of reflectance measurements on a Ge-Al₂O₃ film, $2.8\text{ }\mu\text{m}$ thick, containing 35 vol% Ge and sputtered on an aluminum mirror. The structure is absorbing for wavelengths below the absorption edge of Ge. Because of the low dielectric constant of Al₂O₃ compared with that of Ge²² the reflectance of the film at $\lambda < 1.2\text{ }\mu\text{m}$ is 0.2, which is appreciably lower than the reflectance (~ 0.4) corresponding to a nongranular Ge film.

The experimental results are compared with calculations based on the published optical constants of amorphous germanium²² and Al₂O₃ using Eqs. (1) and (2). As can be seen in Fig. 7, the agreement between experiment and the Maxwell-Garnett theory is excel-

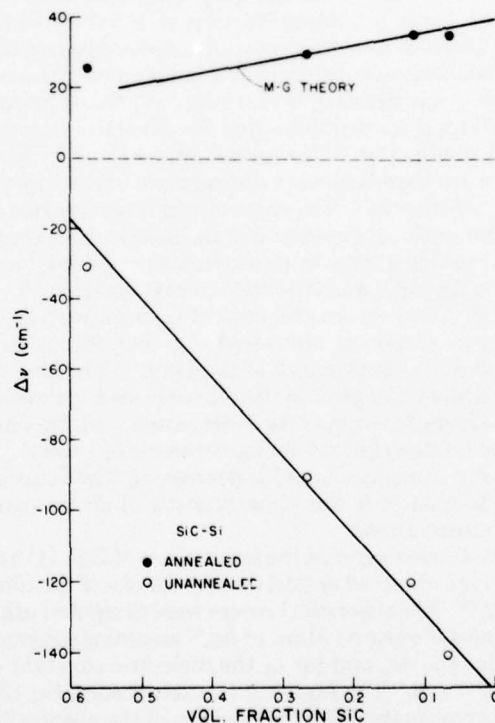


Fig. 6. Wavenumber shift $\Delta\nu$ of the reststrahlen absorption peak in Si-SiC as a function of volume fraction of Si-SiC, before and after annealing. The straight line for the annealed samples was computed from Eq. (2).¹⁹

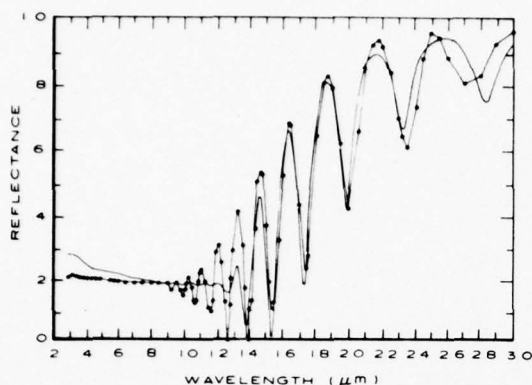


Fig. 7. Reflectance of a 2.8- μm thick film of Ge- Al_2O_3 containing 35 vol% Ge, deposited on Al. Experimental data are given by the solid circles connected by straight lines. The solid curve was computed using Eq. (2). (After Gittleman.²)

lent; equally good fit (not shown in Fig. 7) was obtained using Eq. (1). Thus in the case of the absorption edge of a granular semiconductor it is not possible to discriminate between the two theories.

V. Practical Applications

The technological importance of composite systems stems from the fact that it is possible to combine the characteristics of two or more components and produce materials with entirely new properties. This extra degree of freedom allows one to tailor optical materials for specific applications.

A technology where composite materials are expected to play an important role is in photothermal conversion of solar energy. This application requires a highly selective solar absorber that has a high absorptivity in the spectral region of the sun (emissivity $\epsilon_{\text{em}} \approx 1$ for wavelength $\lambda \lesssim 1.5 \mu$) and is a good reflector in the spectral region $\lambda \gtrsim 1.5 \mu$ ($\epsilon_{\text{em}} \approx 0$). Such highly selective characteristics cannot be achieved in a single material. To overcome this problem it has been proposed that a semiconductor film with an absorption edge in the $1 \sim 2 \mu$ range on top of a highly reflecting metal be used.²³ This tandem structure has the low emissivity of the metal at long wavelength (because the semiconductor is transparent), while in the solar spectral region it has the absorption characteristic of the semiconductor. The difficulty with this structure is that the semiconductor (with the required low energy gap) invariably has a high index of refraction. Thus an appreciable fraction of the solar energy is reflected, which results in a reduction in the performance of the converter. An effective method reducing the reflectance is to make use of a granular semiconductor. As was pointed out by Gittleman,² the index of refraction of a granular semiconductor can be made quite small while retaining the absorption characteristic of the semiconductor. It was estimated² that the performance of a granular semiconductor selective absorber using Ge grains is expected to approach 80% of the ideal performance.²³ This represents a large improvement over the converter using a nongranular semiconductor.

Other optical applications of granular metals that have been proposed include: tuned filters,^{14,15,24} where use is made of the absorption peak at λ_A ; neutral filters²⁵; granular metals with an electrooptic dielectric in which it may be possible to modulate λ_A by an external electric field²⁴; and an optical strain gauge that utilizes the effect of strain on ϵ_s .²⁴

We thank H. A. Weakliem, Jr., and P. J. Zanzucchi for use of unpublished data and G. D. Cody for helpful suggestions. This research was supported in part by the U.S. Air Force Office of Scientific Research (AFSC) under contract F44620-75-C-0057. This paper was presented at the OSA Topical Meeting on Optical Interference Coatings, Asilomar, Calif., 24 February 1976.

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Comparison of the Effective Medium and the Maxwell-Garnett Predictions for the Dielectric Constants of Granular Metals

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Reprinted from Physical Review B, Vol.15, No.6, 15 March 1977

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Comparison of the effective medium and the Maxwell-Garnett predictions for the dielectric constants of granular metals*

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(Received 29 April 1976)

It is shown that, in the case of granular metals, the Maxwell-Garnett theory provides a good approximation to the dielectric constant of granular metals, while the effective-medium theory does not apply.

In a recent paper Stroud¹ has shown that the effective-medium theory² (EMT) and the Maxwell-Garnett theory³ (MGT) can be obtained as different approximations to a generalized transport theory of composite systems.

In this note we compare the predictions of the two theories with experiment for the case of granular metals.⁴⁻⁷ These materials⁸ consist of metal dispersions such as colloids,⁴ cermets,^{5,6} and discontinuous metal films.⁷ Granular metals exhibit a strong absorption peak in the optical region which is absent in the bulk metal. An example of this is given by Au colloidal particles suspended in glass in which the absorption peak gives rise to a characteristic ruby-red color.

In the derivation of the MGT and EMT it is assumed that the composite material consists of grains that are much smaller than the wavelength of light, but are large enough so that they can be characterized by macroscopic dielectric constants. Approximate solutions to the integral equation from which the dielectric constant is determined are obtained by neglecting multiple scattering of the electric field by the grains.¹ This approximation is equivalent to a mean-field theory in which the effect of all the grains on a given grain is represented by a uniform field. In the EMT approximation the two components, *A* and *B*, of the granular metal are treated in an equivalent manner. Grains of *A* and *B* are assumed to be embedded in an effective medium whose dielectric constant is ϵ_s , the same as that of the composite material. The choice of the dielectric constant of the effective medium is such that the average

field acting on a grain due to all the other grains averages to zero. The dielectric constant of the composite system ϵ_s in the case where grains of *A* and *B* are spherical is given by the relation¹

$$x \frac{\epsilon_A - \epsilon_s}{\epsilon_A + 2\epsilon_s} + (1-x) \frac{\epsilon_B - \epsilon_s}{\epsilon_B + 2\epsilon_s} = 0, \quad (1)$$

where *x* is the volume fraction of component *A*, and ϵ_A and ϵ_B are the dielectric constant of the individual grains.

In the MGT approximation it is assumed that the grains of one component are embedded in the matrix of the other component. This theory, unlike the effective-medium theory, treats the two components in an asymmetric manner. The field acting on a grain due to all the other grains, is assumed to be given by the Lorentz local field. The expression for ϵ_s , generalized to the case where the grains of *A* (embedded in matrix *B*) are rotational ellipsoids identical in shape and orientation (but not necessarily in size), is given by⁵

$$\frac{\epsilon_s - \epsilon_B}{L\epsilon_s + (1-L)\epsilon_B} = x \frac{\epsilon_A - \epsilon_B}{L\epsilon_A + (1-L)\epsilon_B}, \quad (2)$$

where *L* is the characteristic depolarization factor. For spherical grains ($L = \frac{1}{3}$) Eq. (2) reduces to the usual Maxwell-Garnett result.³

Inspection of Eqs. (1) and (2) shows that their forms are entirely different: Eq. (1) is quadratic in ϵ_s and symmetric in ϵ_A and ϵ_B while Eq. (2) is linear in ϵ_s and asymmetric in ϵ_A and ϵ_B . The different ways in which the two theories treat the components *A* and *B* lead to gross differences in the predicted optical properties. We illustrate

this for two cases: a hypothetical granular metal consisting of isolated spherical grains of a Drude metal, dispersed in a dielectric medium with a dielectric constant of unity,⁹ and for the case of a granular Ag film. In Fig. 1 is given the MGT dielectric constant [Eq. (2)] for the Drude metal dispersion. It should be noted that its behavior is analogous to that of the dielectric constant of ionic crystals near the reststrahlen band. As the volume fraction of the metal increases, the ampli-

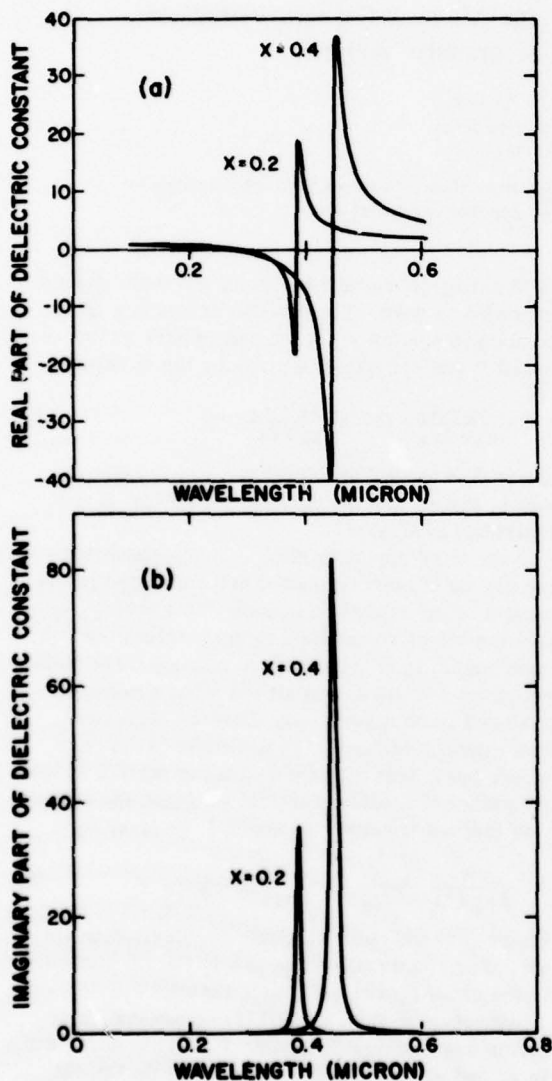


FIG. 1. MGT dielectric constant ϵ_s of spherical metal grains in vacuum for two different volume fractions of the metal, x ; calculated from Eq. (2) assuming $\epsilon_B=1.0$ and for ϵ_A the complex dielectric constant of a Drude metal with a plasma frequency of $1.5 \times 10^{15} \text{ sec}^{-1}$ and a relaxation time of $1 \times 10^{-14} \text{ sec}$; (a) real part, and (b) imaginary part of the dielectric constant.

tude of the anomaly in ϵ_s grows, and the wavelength λ_A at which the anomaly occurs moves to larger values. Figure 2 shows the dielectric constant of the same Drude metal dispersion obtained from the EMT [Eq. (1)]. The behavior of ϵ_s is in this case very different. For $x=0.4$, the real part of ϵ_s is metal-like (negative at long wavelength and changing sign at the plasma frequency) and for $x=0.20$ it is insulatorlike (positive at all wavelengths). The transition from metallic to dielectric behavior takes place at $x=\frac{1}{3}$.

In Fig. 3 are compared the computed and measured optical densities of an Ag-SiO₂ film. The theoretical curves were computed using for ϵ_A the complex dielectric constant of Ag,¹⁰ and for ϵ_B the dielectric constant of SiO₂ ($\epsilon_B=2.2$) and the experimental points from the work of Cohen *et al.*⁵ The MGT [Eq. (2)] predicts reasonably well the position of the observed absorption peak (λ_A) although the predicted height of the peak is larger than observed. In addition, the MGT predicts correctly the compositional variation of the

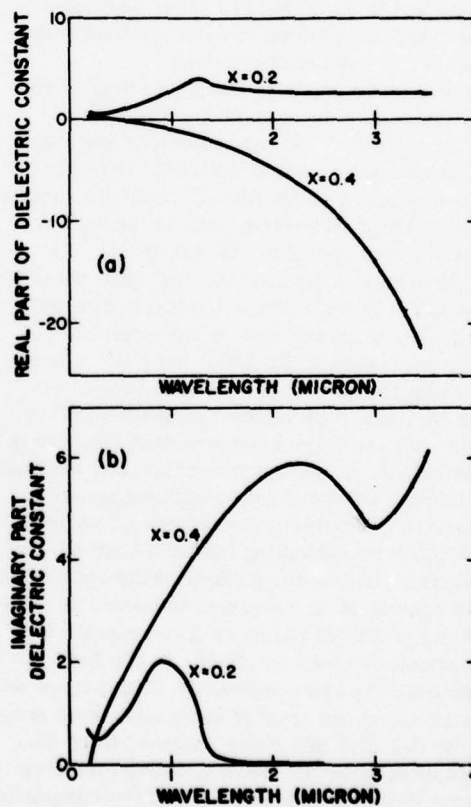


FIG. 2. EMT dielectric constant of spherical metal grains in vacuum; calculated from Eq. (1) using the same parameters as in Fig. 1; (a) real part, and (b) imaginary part of the dielectric constant.

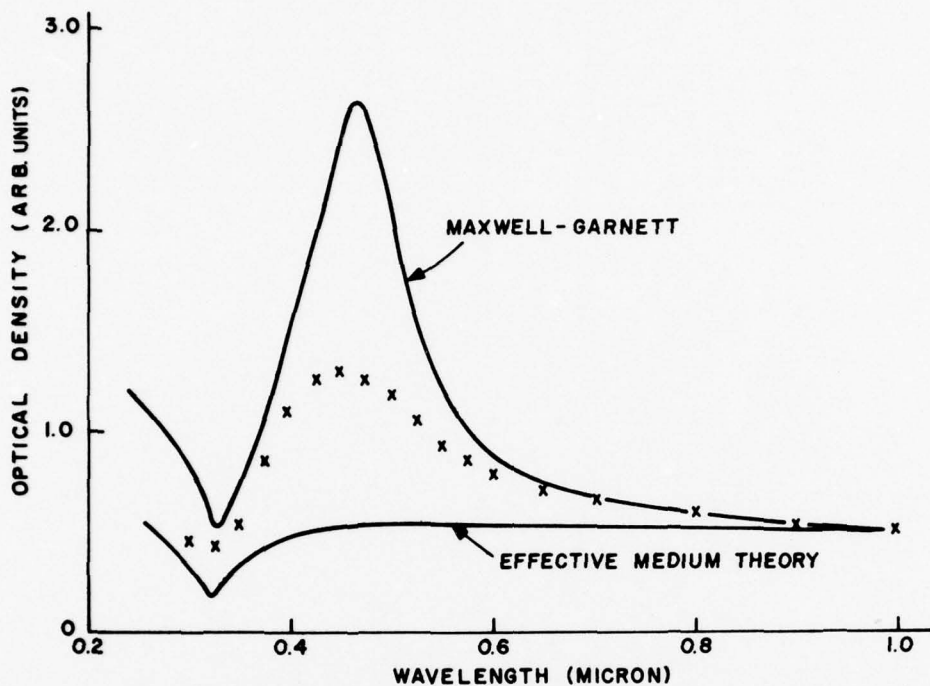


FIG. 3. Optical density of Ag-SiO₂ film containing 0.39 vol. fraction Ag. Theoretical curves computed from Eqs. (1) and (2); experimental datapoints (Ref. 5) are represented by crosses. The optical densities have been normalized at 1 μ m.

plasmas resonance in granular metals,⁶ i.e., a shift to longer wave lengths as the volume fraction of the metal is reduced. Similarly good agreement with the theory is obtained for other granular metals^{4,7} in which the metal grains are isolated.

On the other hand, the EMT result is strikingly different from experiment in that it yields no distinctive absorption peak (see Fig. 3). Calculations using Eq. (1) show that for $x=0.39$ the plasma wavelength is about 1 μ m and is increasing very rapidly with decreasing x indicating approach to a metal-nonmetal transition. This variation of the

plasma frequency is very different from experimental observation.⁶ We therefore conclude that the EMT is not applicable to metal dispersions while the MGT provides a reasonably good description of the dielectric constant of such systems.

ACKNOWLEDGMENT

We wish to thank G. D. Cody for helpful suggestions and discussions.

*Research supported in part by Air Force Office of Scientific Research (AFSC) under Contract No. F44620-75-C-0057.

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Electrochromism in the Composite Material Au-WO_3

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Reprinted from Applied Physics Letters, Vol. 31, No. 2, 15 July 1977

RCA LABORATORIES PRINCETON, NEW JERSEY



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Electrochromism in the composite material Au-WO₃ ^{a)}

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We have produced for the first time an electrochromic cermet composed of Au grains dispersed in the electrochromic WO₃. The electrochromism arises from a shift in the wavelength of the dielectric absorption characteristic of gold cermets. The shift is due to a change in the dielectric constant of the WO₃ matrix as a result of the coloring process. This is to be contrasted with the coloring in pure WO₃, which results from the appearance of a broad absorption band in the red and infrared.

PACS numbers: 42.70.Fh, 81.20.Nd, 77.55.+f, 78.65.Jd

The electrochromic material WO₃ can be colored by double injection of protons and electrons forming H_xWO₃.¹ The coloring results from the appearance of a broad absorption band in the red and infrared.² Its blue color is believed due to electrons hopping between W⁵⁺ and W⁶⁺ sites³ although another related mechanism has recently been proposed.^{4,5} In this work we have colored all the samples by the technique of Crandall and Faughnan.¹

We prepared specimens of pure WO₃ by rf sputtering from a yellow-compressed-powder 7.62-cm-diam WO₃ target in the presence of a controlled oxygen leak of 1.2×10^{-3} to 2.9×10^{-3} Torr in an argon pressure of 5×10^{-2} Torr. The exact wavelengths and shape of the absorption band of WO₃ were found to depend on sputtering conditions with the substrate temperature the most important variable. The absorption band of WO₃ films is either near 0.8 μ or 1.4 μ depending on sample crystallinity. The temperature of deposition determines whether the sample is amorphous or crystalline. The effect of crystallinity on the absorption band has been reported by Schirmer *et al.*⁴ Figure 1 shows the optical density of a plain WO₃ film, uncolored and colored, prepared under the conditions used for all the films reported here, including Au-WO₃. As can be seen there is some coloration present even in the "uncolored" sample, as evi-

denced by the relative maximum in the optical density at 0.8 μ m.

The Au-WO₃ films were prepared by placing a 1.27-cm-disk of Au on the edge of the 7.62-cm WO₃ sputtering target and sputtering a film onto a glass or quartz substrate with a transparent electrode. The sputtering technique is similar to that used by Hanak *et al.*⁶ to produce a wide range of cermet compositions.

As prepared, the cermet film appears blue in transmission. At low Au concentrations the film is transparent and pale blue, at higher Au concentrations the film has a metallic luster and is reflecting. When

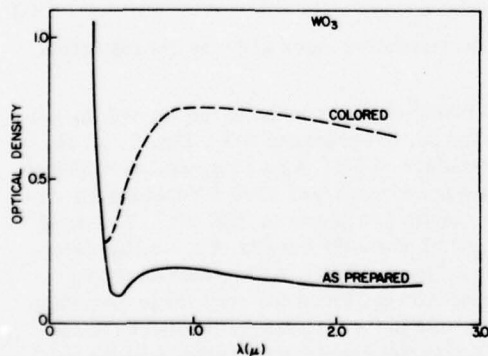


FIG. 1. Optical density of pure sputtered WO₃ ~1000 Å thick as prepared (uncolored, solid curve) and colored (dashed curve).

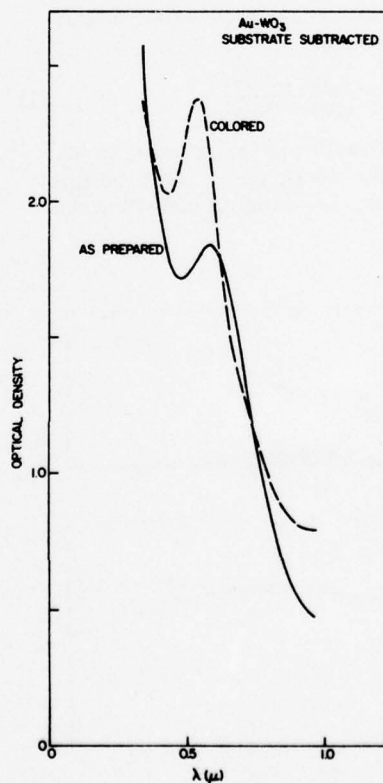


FIG. 2. Optical density of ~2000-Å-thick film as-prepared (uncolored, solid curve) and colored (dashed curve) sputtered Au-WO₃ cermet, 25 at.% Au. Film is deposited on a transparent electrode. The optical density of the substrate and transparent electrode has been subtracted. The uncolored film has an absorption peak at 5900 Å and the colored film at 5400 Å.

^{a)}Research sponsored by the Air Force Office of Scientific Research (AFSC), U.S. Air Force, under Contract F44620-75-C-0057.

colored, the films appear red in transmission. The color is a faint pink at low Au concentrations and a strong red near 25 at. % Au. At high Au concentrations the reflectivity is too great to see a change of color in transmission. Figure 2 shows the optical density measured on a Cary 14 spectrophotometer of a 25 at. % Au in WO_3 film uncolored and colored. The peaks in the optical density at 5900 and 5400 Å are responsible for the blue and red appearance of the uncolored and colored films, respectively. As the % Au decreases, the peaks become less pronounced and broader but do not shift in wavelength. A similar absorption peak is well known in the case of sputtered films of Au and SiO_2 ⁷ and has been explained by applying the model of Maxwell-Garnett⁸ (M-G).

The optical constants (n, k) of sputtered films of WO_3 have been determined for both the uncolored and the colored states from transmittance and reflectance measurements. The results are shown in Fig. 3. The minimum in n as a function of wavelength is a direct consequence of the minimum in the optical density, Fig. 1, of both the as-prepared and colored films. In the case of the as-prepared films, the residual coloration is responsible for this structure which is absent in the values of n reported by Faughnan *et al.*³ for evaporated uncolored WO_3 .

The optical density of the Au- WO_3 cermet can be examined using the M-G theory as has been done for Au- SiO_2 cermet.⁷

In the case of metal spheres in a dielectric matrix, the M-G relation is given by

$$\frac{\epsilon(\omega) - \epsilon_i(\omega)}{\epsilon(\omega) + 2\epsilon_i(\omega)} = (1-x) \frac{\epsilon_m(\omega) - \epsilon_i(\omega)}{\epsilon_m(\omega) + 2\epsilon_i(\omega)}, \quad (1)$$

where x is the volume fraction of insulator, ϵ_m is the dielectric constant of the metal, and ϵ_i is the dielectric constant of the insulator. The complex dielectric con-

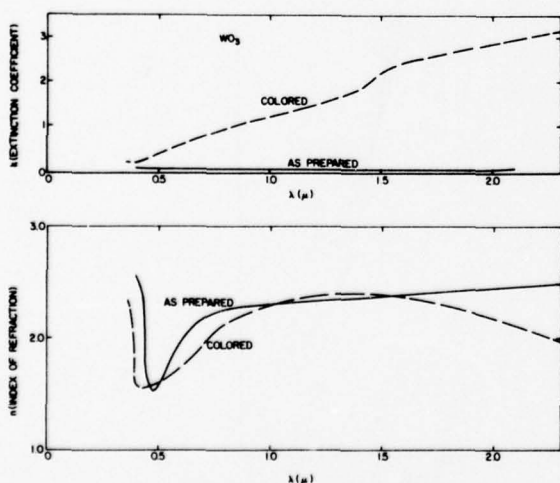


FIG. 3. Extinction coefficient k and index of refraction n of sputtered films of pure WO_3 calculated from transmission and reflection data. Solid line is for uncolored film. Dashed line is for colored film.

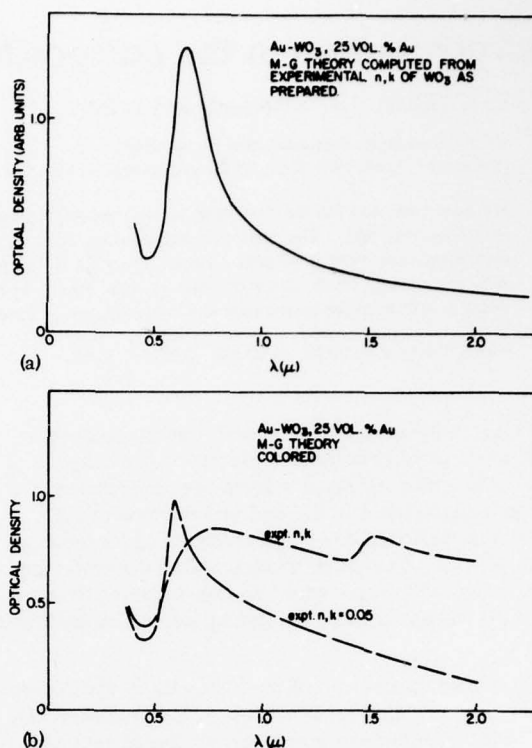


FIG. 4. (a) Computed optical density of uncolored Au- WO_3 cermet, 500 Å thick, 25 vol% Au. M-G calculation using experimental values of n and k for uncolored WO_3 . Absorption peak is at 6400 Å. (b) Computed optical density of colored Au- WO_3 cermet, 500 Å thick, 25 vol% Au. M-G calculation using experimental values of n and k and also using experimental n and $k = 0.05$. In the latter case, absorption peak is at 6000 Å.

stant of the cermet can be written

$$\epsilon = \epsilon_1 + i\epsilon_2, \quad (2)$$

where

$$\epsilon_1 = n^2 - k^2 \quad (3)$$

and

$$\epsilon_2 = 2nk, \quad (4)$$

where n is the refractive index and k is the extinction coefficient.

Using published⁹ optical constants for Au and the values of (n, k) for our as-prepared WO_3 , Fig. 3, an absorption is obtained at 6400 Å as compared with 5900 Å observed for our cermet (and 5500 Å reported for Au- SiO_2 ⁷). The results are shown in Fig. 4(a). The solid curve of Fig. 4(b) gives the results of a similar calculation for the colored cermet. These results do not agree with observation. Since the very large extinction coefficient seemed the most reasonable source of disagreement, it was arbitrarily suppressed and the calculation was repeated. As can be seen from the dashed curve of Fig. 4(b), qualitative agreement is restored.

It should be noted that the absorption peak is sharpened when k is suppressed and is "blue" shifted from the absorption in the uncolored cermet by about 400 Å in agreement with experiment. All that is required of

the WO_3 matrix for a blue shift to result from Eq. (1) is (1) for n (and hence the dielectric constant) of the colored state to be less than n of the as-prepared state at wavelengths near the anomaly; (2) for k not to be so large as to wash out the anomaly altogether. It is the latter observation that suggests to us that the presence of the Au or the structure of WO_3 in the cermet prevents coloration in the cermet to proceed to the same degree as in the pure WO_3 films.¹⁰

In conclusion, by combining the electrochromic material WO_3 with a fine dispersion of Au grains we have created a novel electrochromic material. The optical properties of this new material can be partially described by the M-G theory in which the optical constants of the matrix material, WO_3 , change under coloration. We conclude that the optical constants of the WO_3 itself are modified by the Au inclusions in the colored state.

We would like to thank R.S. Crandall and B.W. Faughnan for many valuable discussions; D.G. Fisher, J.T. McGinn, R.J. Paff, and H.H. Whitaker for their

sample analysis studies, and E.F. Hockings for instruction in the use of ellipsometry.

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OPTICAL PROPERTIES AND SELECTIVE SOLAR ABSORPTION OF COMPOSITE MATERIAL FILMS*

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(Received March 31, 1977; accepted April 8, 1977)

Composite material films are widely used as selective solar absorbers. We investigated the cermet Au-MgO and W-MgO and the semiconductor-insulator composites Si-CaF₂ and Si-MgO prepared by co-sputtering. For Au-MgO the dielectric constant does not exhibit the resonance structure near 0.6 μm that is characteristic of other systems of gold particle dispersions, and furthermore the infrared absorption is much larger than that predicted by theory. This anomalous behavior could be due to the textured surface of the films. For the W-MgO films the observed dielectric constants are in good agreement with the Maxwell Garnett theory. In the films with Si dispersions strong absorption bands appear in the infrared; these are due to compounds formed by chemical reaction between Si and the matrix materials. The photothermal conversion efficiency of solar energy of these materials was estimated and compared with other selective solar absorbers.

1. INTRODUCTION

Coatings for the selective absorption of solar energy which are used commercially are mostly composite materials¹⁻³. For example, electroplated chrome black—one of the most effective and widely used solar coatings—consists of a graded composite of chromium and chromium oxide^{2,4}. In many cases the composition and microstructure of these coatings is not well characterized, and the physical processes which are responsible for their high spectral selectivity are not well understood yet. To gain a better understanding of these materials, it is advantageous to study simpler composite systems which can be well characterized. With this in mind we chose to investigate the cermets Au-MgO and W-MgO and the semiconductor-insulator composites Si-CaF₂ and Si-MgO.

Cermets consisting of small metal grains dispersed in a dielectric have optical characteristics suitable for selective solar absorption: at optical wavelengths they are absorbing because of interband transitions and plasma resonance absorption of the metal grains; in the IR their absorption is low provided the dielectric is transparent. A suitable insulator material which is transparent in the thermal IR is MgO. The Au-MgO cermets are interesting because recently Fan and Zavracky⁵

* Paper presented at the International Conference on Metallurgical Coatings, San Francisco, California, U.S.A., March 28-April 1, 1977.

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found that this system exhibits an absorption at optical wavelengths that is greatly in excess of that observed for other gold particle dispersions. The W-MgO system represents an example of a transition metal cermet, and its study is relevant to the understanding of the spectral selectivity of metal composites such as electroplated nickel and chrome blacks. Silicon is attractive for selective solar absorption because its absorption edge is near 1 μm . The reason for dispersing Si in an insulating matrix of low dielectric constant is to reduce the large index of refraction and hence the reflectance of silicon films^{6,7}.

2. CHARACTERIZATION OF FILMS

Films of W-MgO, Au-MgO, Si-CaF₂ and Si-MgO were prepared by r.f. sputtering from composite targets^{8,9} of W, Au, Si and the insulators MgO and CaF₂. The compositions of the films were determined from chemical analysis. IR absorption measurements of the cermets deposited on Si or KBr showed the characteristic absorption band of MgO at 25 μm ; from the absence of any additional absorption bands in the IR it was inferred that no appreciable reaction takes place between the metals and MgO. However, for the Si-MgO and Si-CaF₂ composites, strong additional absorption bands were observed, indicating some chemical reaction between Si and the molecules of the insulators.

A transmission electron micrograph of an Au-MgO film is shown in Fig. 1. The

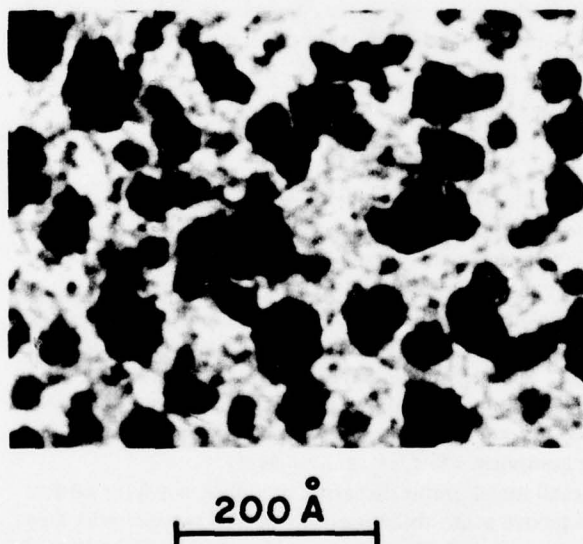


Fig. 1. A transmission electron micrograph of an Au-MgO cermet film 140 Å thick containing 25 vol. % Au and deposited on a carbon substrate.

film has a distribution in grain sizes ranging from 70 Å down to the resolution limit of the microscope (3 Å). In the W-MgO films the W grains were 5–10 Å in size. The diffraction patterns indicated crystalline Au and MgO grains. The fact that the

MgO is crystalline in sputtered metal-MgO cermets has also been observed by Fan and Henrich¹⁰.

Scanning electron micrographs revealed that the Au-MgO films had very rough surfaces, while the W-MgO films were quite smooth. An electron micrograph of an Au-MgO film 1500 Å thick is shown in Fig. 2; it shows a surface roughness on

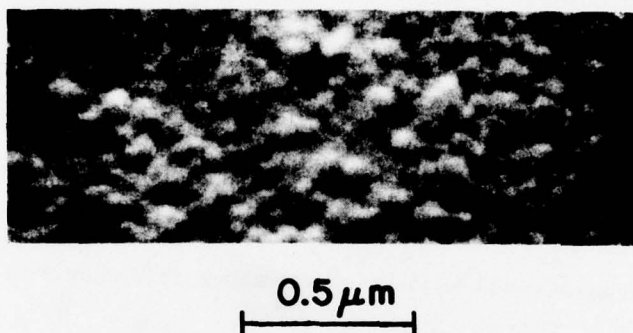


Fig. 2. A scanning electron micrograph of an Au-MgO cermet film 1500 Å thick containing 25 vol. % Au and deposited on a sapphire substrate; the electron beam is at 45° with respect to the film normal.

a scale of about 2000 Å. We believe that it is this surface roughness which is responsible for the unusual optical properties of the Au films; this is discussed in more detail in Section 3. The formation of the surface roughness is believed to be associated with the high secondary electron emission of MgO which can result in peculiar sputtering effects¹¹. The different behavior of the Au-MgO and W-MgO films may be related to the high sputtering rate of Au compared with that of W (Au has a sputtering rate 5 times larger than W).

3. MAXWELL GARNETT THEORY

To interpret the optical measurements we used the Maxwell Garnett (MG) theory¹² which relates the optical constants of the composite material to those of the metal and the insulator¹³. This theory has been shown to predict correctly the position of the absorption peaks in the visible characteristic of Au and Ag metal dispersions such as discontinuous metal films¹⁴, colloidal particles¹⁵ and cermets¹³. According to the MG theory, the complex dielectric constant ϵ of the composite material is given by

$$\frac{\epsilon - \epsilon_i}{\epsilon + 2\epsilon_i} = x \frac{\epsilon_M - \epsilon_i}{\epsilon_M + 2\epsilon_i} \quad (1)$$

where ϵ_M and ϵ_i are the dielectric constants of the metal and insulator respectively and x is the volume fraction of the metal. In eqn. (1) it is assumed that the metal grains are spherical and are surrounded by the insulator.

The metal dielectric constant can be separated into two parts, $\epsilon_M = \epsilon_B + \epsilon_D$, where ϵ_B is the interband contribution and ϵ_D is the Drude contribution. The Drude

part is given by

$$\epsilon_D = 1 + \frac{\omega_p^2 \tau}{i\omega(1 + i\omega\tau)} \quad (2)$$

where ω is the angular frequency of the light, ω_p is the plasma frequency and τ is the mean scattering time of the conduction electrons.

4. OPTICAL PROPERTIES

The refractive index n and the extinction coefficient k of the films were determined from the measurements of normal transmittance and reflectance of the films deposited on sapphire substrates, using a method similar to that described by Bennett and Booty¹⁶.

4.1. Au-MgO

Figure 3 shows the values of n and k before and after annealing as a function of

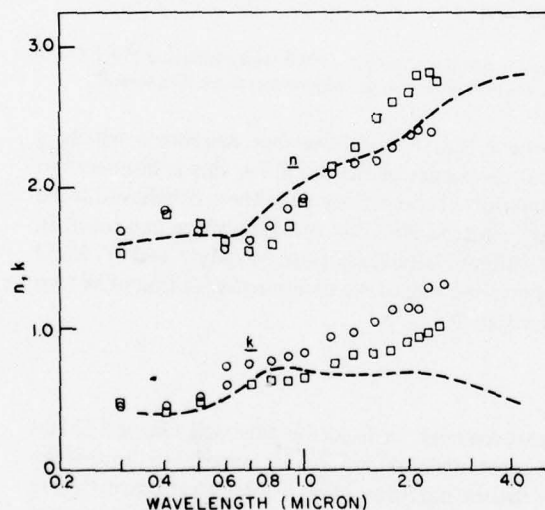


Fig. 3. The optical constants as a function of wavelength for a 1500 Å Au-MgO cermet film containing 25 vol. % Au deposited on sapphire: ---, from Fan and Zavracky⁵; □, annealed; ○, as prepared.

λ , for an Au-MgO film containing 25 vol. % Au. The results are similar to those reported by Fan and Zavracky⁵. In Fig. 4 the experimental values of the real part ϵ_1 ($= n^2 - k^2$) and the imaginary part ϵ_2 ($= 2nk$) of ϵ are compared with the values computed from eqn. (1). The published values of the optical constants of MgO¹⁷ and those of Au¹⁸ modified for several values of τ according to eqn. (2) were used. The theory predicts a pronounced structure in ϵ_1 and ϵ_2 at about 0.6 μ m due to plasma resonance absorption in the Au grains; however, experimentally this structure is barely perceptible. It is noteworthy that, in other systems of Au particle dispersions, characteristic plasma resonance structure is observed¹³⁻¹⁵.

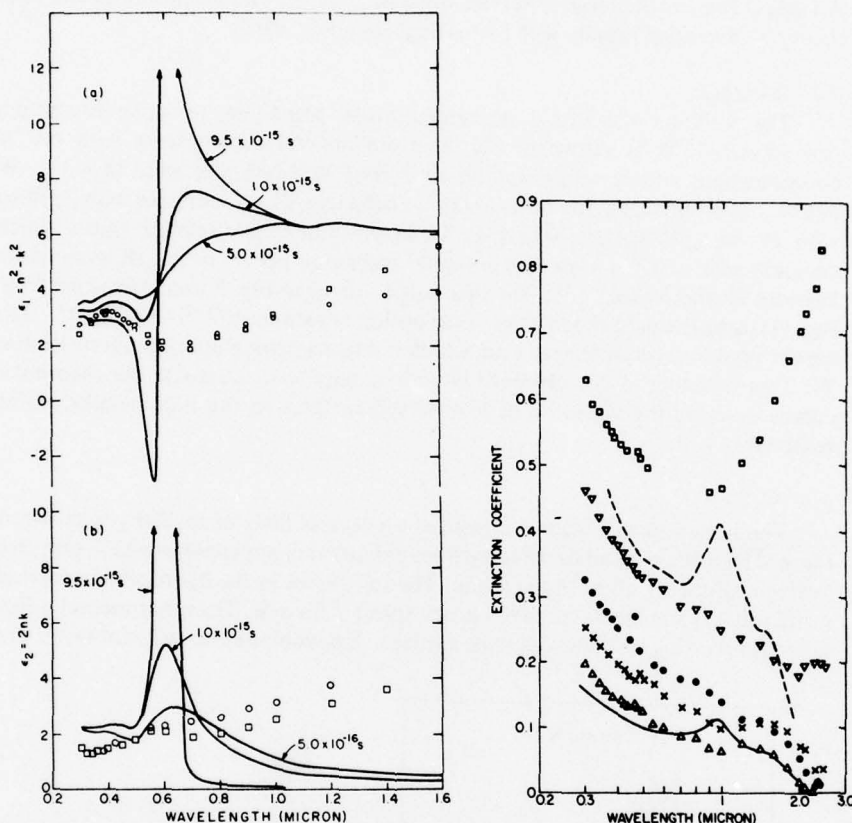


Fig. 4. The dielectric constant of the Au-MgO cermet in Fig. 3 plotted against the wavelength giving (a) the real part ϵ_1 and (b) the imaginary part ϵ_2 : —, calculated for the indicated electron scattering times using eqn. (2) and the published data for Au¹⁸ and MgO¹⁷ from MG theory; \square , annealed; \circ , as prepared.

Fig. 5. The extinction coefficient k for W-MgO cermet of various volume percentages of W: Δ , 13 vol. % W; \times , 16 vol. % W; \bullet , 19 vol. % W; ∇ , 28 vol. % W; \square , 34 vol. % W; the curves were calculated using eqn. (1) and the published data for W²⁰ and MgO¹⁷ from MG theory for 10 vol. % W (—) and 30 vol. % W (---); the films were about 1500 Å thick.

The absence of the structure in the Au-MgO films cannot be explained on the basis of small grain size. A mean free path l of 10 Å corresponds to a relaxation time τ ($= l/v_F$ where v_F is Fermi velocity) of about 5×10^{-16} s. However, as can be seen in Fig. 4, even with such a low value of τ the theoretical curves still exhibit a characteristic structure near 0.6 μ m; moreover there are an appreciable number of grains larger than 10 Å in the films (see Fig. 1). A possible explanation for the absence of the structure is the surface roughness of the films (Fig. 2), which could give rise to strong absorption over a wide range of wavelengths and thus smear out the structure. The effects of surface roughness and compositional gradient are discussed by Stephens and Cody¹⁹. One other anomalous characteristic of the

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Au-MgO films is the large observed value of ϵ_2 in the IR; according to the MG theory, ϵ_2 decreases rapidly with increasing λ (see Fig. 4(b)).

4.2. W-MgO

The variation of k with λ determined on W-MgO films for different volume percentages of W is shown in Fig. 5. n did not vary appreciably with the W concentration, and its value was about 2. The W-MgO film with 34 vol. % W behaves as a metal, having an extinction coefficient which increases with λ ; films with 28 vol. % W or less behave as insulators—they have small k values which decrease with λ . Thus a metal-non-metal transition occurs in the IR somewhere between 28 and 34 vol. % W. The theoretical curves in Fig. 5 were computed from eqn. (1) using the published values of the optical constants of W²⁰ and MgO¹⁷. The curves exhibit a structure near 1 μ m which is due to a strong interband transition in W. This structure is not observed experimentally, but otherwise the theoretical curves describe the behavior of k observed in films in the non-metallic region reasonably well.

4.3. Si-CaF₂

The variation of k with λ measured on several films of Si-CaF₂ is shown in Fig. 6. The refractive indices of these films did not vary appreciably with λ , and their average values are given in the figure. The full curves in the figure were computed using eqn. (1) and the data of Pierce and Spicer²¹ for a-Si. The experimental results differ appreciably from the calculated values. A possible explanation for this is that

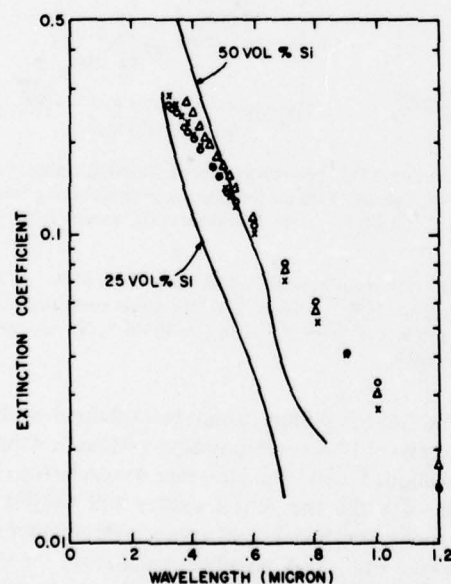


Fig. 6. The extinction coefficient k for several Si-CaF₂ composites; O, 15 vol. % Si, $n = 1.6$; \times , 24 vol. % Si, $n = 1.7$; Δ , 29 vol. % Si, $n = 1.8$; the curves were calculated from eqn. (1), using published data for Si²¹ and CaF₂²⁶.

the a-Si grains in our specimens differed in structure from the a-Si used in the experiments of Pierce and Spicer²¹.

5. SOLAR PERFORMANCE

In photothermal conversion of solar energy, the power that can be delivered to a load is the difference between the solar power absorbed by the absorber and the power which is lost by radiation, convection and conduction. If we take into account only heat radiation losses from the absorber, the conversion efficiency η can be expressed in terms of the hemispherical spectral reflectance $R(\lambda, T)$ at the operating temperature T of the absorber:

$$\eta = \frac{\alpha \int S(\lambda) \{1 - R(\lambda, T)\} d\lambda - \int W(T, \lambda) \{1 - R(\lambda, T)\} d\lambda}{\alpha \int S(\lambda) d\lambda} \quad (3)$$

where $S(\lambda)$ is the spectral energy density of the sun, $W(T, \lambda)$ is the spectral radiation energy density of a black body at temperature T and α is the concentration factor of the sun. For the ideal photothermal converter, R is zero for $0 < \lambda < \lambda_c$ and unity for $\lambda \geq \lambda_c$. The cut-off wavelength λ_c is that wavelength at which the incident solar energy density is equal to the radiant energy density of a black body. For a 500 °C black body $\lambda_c \approx 1.5 \mu\text{m}$.

In order to compare the values of η for different composite films, we replace $R(\lambda, T)$ in eqn. (3) by the normal reflectance R_n at room temperature. It should be noted that this substitution can result in error because it does not take into account the temperature dependence of $R(\lambda, T)$ and the effects of surface structure on the angular dependence of the reflectivity.

Selective solar absorbers were made by coating W mirrors with the composite films. The results of measurements of the normal reflectance R_n of the absorbers are given in Figs. 7 and 8. The strong absorption band at $12 \mu\text{m}$ for Si-CaF₂ (Fig. 7) is

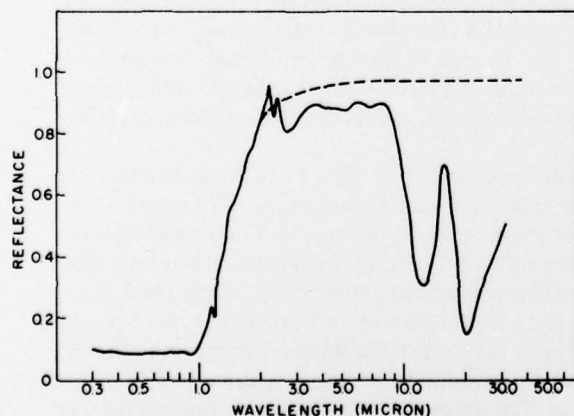


Fig. 7. A reflectance vs. wavelength plot for an Si-CaF₂ composite film 5 μm thick on an Al mirror: ---, expected reflectance on the assumption of no chemical reaction.

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believed to be due to IR absorption of molecules formed by chemical reaction between Si and CaF_2 to form CaSiF_6 . Strong absorption bands were also observed for Si-MgO and were probably due to the formation of magnesium silicate.

The W-MgO film with 34 vol. % W, whose reflectance is given in Fig. 8.

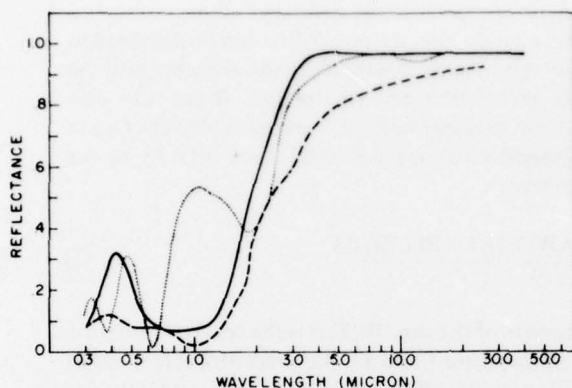


Fig. 8. A reflectance vs. wavelength plot: ---, 25 vol. % Au-MgO cermet on Mo (after Fan and Zavracky⁵); 34 vol. % W-MgO cermet (1500 Å) on W; —, Zr-N_x on Ag (after Blickensderfer *et al.*²⁴).

exhibited the largest solar selectivity of the W-MgO films. Pronounced interference fringes are present because of the small extinction coefficient of the film. It is interesting to compare these results with the reflectance of electroplated chrome black. Chrome black is a chromium-chromium oxide composite^{2,4}, and we would expect it to have similar values of k and n to those of W-MgO (W and Cr have similar optical constants). The fact that chrome black coatings have a much higher solar absorption than W-MgO films is a likely consequence of the fact that the chrome black coatings have a rough surface²² and a graded composition²³. The effect of surface roughness could also be the explanation for the low reflectance and the absence of interference fringes below 1.5 μm in the Au-MgO cermet (Fig. 8). We have also included in Fig. 8 the zirconium-zirconium nitride absorber of Blickensderfer *et al.*²⁴ as another example of a metal-insulator composite absorber. While no structural characterization is reported, it is likely that these films are multi-phase composites.

The conversion efficiencies η of the absorbers in Figs. 7 and 8, calculated from eqn. (3) assuming one standard air mass, are plotted against the solar concentration factor α in Figs. 9 and 10 for two operating temperatures—150 °C as an appropriate temperature for residential applications and 500 °C for driving a steam turbine. For comparison we have included the η corresponding to Honeywell chrome black²⁵. In Fig. 10 two sets of values of η are given for the Si- CaF_2 absorber: one corresponds to the measured IR reflectance (Fig. 7, full curve); the other corresponds to the IR reflectance (Fig. 7, broken curve) that would be expected if there had been no chemical reaction in the composite. The difference between the two curves for η is striking and emphasizes the deleterious effect that a small amount of IR emissivity has on high temperature performance. This point is also illustrated by the behavior

of Au-MgO and chrome black. At low temperatures (Fig. 9) they are excellent converters, whereas at high temperatures (Fig. 10) their conversion efficiencies are rather poor. The reason for this drop in performance is the excessive emissivity in the IR, resulting from the slow rise in reflectance with λ for $\lambda > 1.5 \mu\text{m}$. The relatively poor performance of W-MgO is largely due to its low absorbance in the visible; a thicker film with a graded composition¹⁹ would probably exhibit a higher conversion efficiency at both 150 and 500 °C. For Zn-N_x the low reflectance below 1.5 μm and the rapid rise at longer wavelengths result in a high conversion efficiency both at low and at high temperatures.

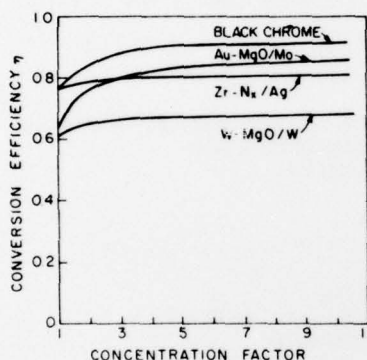


Fig. 9. Photothermal conversion efficiency η vs. the solar concentration factor for composites at 150 °C.

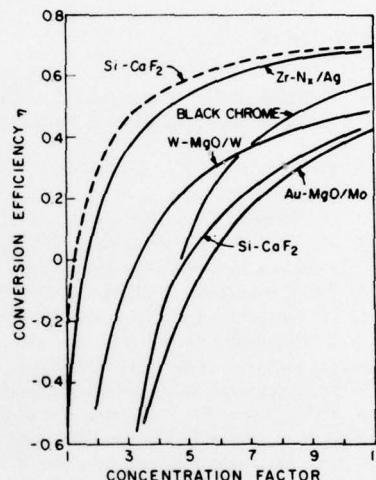


Fig. 10. Photothermal conversion efficiency η vs. the solar concentration factor for composites at 500 °C: —, Si-CaF₂ film, computed using the full curve in Fig. 7 for R_n ; ---, Si-CaF₂ film, computed using the broken curve in Fig. 7 for R_n .

6. CONCLUSIONS

For low temperature operations nickel black and chrome black provide economical photothermal conversion of solar energy and the technology for commercial production exists. At high temperatures, requirements for selective absorbers are more severe, *e.g.* the conversion efficiency becomes very sensitive to the emittance at wavelengths greater than 1.5 μm . Furthermore the higher the operating temperature, the more of a problem thermal stability can become. Semiconductors with an absorption edge near 1.5 μm have near ideal characteristics for selective absorption at high temperatures^{22,26} (Fig. 10) provided that reflectance in the visible can be reduced and provided no lattice absorption bands occur in the IR ($\lambda \lesssim 20 \mu\text{m}$). It is clear that far more materials must be researched in order for photothermal conversion of solar energy at high temperature and with a low concentration factor to become technically feasible.

ACKNOWLEDGMENTS

We wish to acknowledge R. Stephens and G. D. Cody for a discussion of their paper prior to publication. We thank J. McGinn and B. J. Seabury for the electron microscopy, H. H. Whitaker for the chemical analysis and D. A. Kramer and S. Bozowski for assistance with the optical measurements.

This research was sponsored by the Air Force Office of Scientific Research (AFSC), United States Air Force, under Contract F44620-75-C-0057. The United States Government is authorized to reproduce and distribute reprints for governmental purposes notwithstanding any copyright notation hereon.

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APPENDIX III

First Draft of a Paper

Titled: "Transport and Optical Properties
of Electrochromic Au-WO₃ Cermets"

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Transport and Optical Properties of Electrochromic Au-WO₃ Cermet*

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ABSTRACT

The electrochromic cermet Au-WO₃ is composed of grains of Au, approximately 20-120 Å in diameter, embedded in a matrix of amorphous WO₃. The optical properties of the cermet, in its red electrochemically colored state, are different from the optical properties of its two components. The WO₃ matrix does not become highly electrically conducting when colored in the presence of Au grains, but rather remains an insulator. A study of the optical and electrical properties of the cermet as a function of gold concentration is presented.

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INTRODUCTION

We have previously reported^[1] on the composite electrochromic material Au-WO₃. By cosputtering Au with WO₃, we prepared films of WO₃ with Au grains, about 20-120 Å in diameter, embedded in a matrix of amorphous WO₃. As prepared, a film of about 25 vol % Au is blue; when "colored" by the technique of Crandall and Faughnan^[2] it turns pink or red. We believe this effect is due to a change in the index of refraction of the WO₃ matrix in which the Au grains are embedded. It is known^[3,4] that a film of a transparent insulator such as SiO₂ or Al₂O₃ with embedded Au grains will be red or pink due to an optical absorption anomaly. On the other hand, electrochemically "colored" WO₃ has been shown to be conducting^[5], even metallic, when electrochemically colored. In order to explain our observation^[1], we assumed that the optical extinction coefficient, k , remained small in the electrochemically colored WO₃ matrix when Au grains are present. Colored WO₃, by itself, has a large extinction coefficient^[1] consistent with its conducting properties.

In this paper we present evidence that the electronic and optical properties of WO₃ in the presence of finely dispersed Au grains are indeed different from pure WO₃.

MATERIALS PREPARATION

Films were prepared by cosputtering Au metal with WO₃ compressed powder targets or by reactive sputtering with W metal targets. For the electrical measurements, In-Sn oxide or Cr-Au electrodes were evaporated onto quartz slides, and a film of Au-WO₃ was deposited with a continuously varying composition from Au-rich to WO₃-rich, after the procedure of Hanak^[16]. Electron probe microanalysis determined the Au:W ratio, and the vol % Au was computed assuming the density of WO₃ to be 7.16 g/cm³.

OPTICAL PROPERTIES

Films of Au-WO₃, as prepared, are blue due to an absorption band at about 6000 Å. This should not be confused with the electrochromic blue of pure WO₃ which is a broad absorption centered at 1.0-1.5μ depending on

crystallinity^[7]. This is illustrated in Fig. 1. All our optical density spectra were taken on a Cary 14 spectrophotometer. No correction has been made for reflection losses.

When a film of Au-WO_3 is colored with H_2SO_4 and indium, in the first few seconds of contact with the indium the blue color intensifies and within minutes the blue changes to pink or red. Figure 2 shows the optical density as a function of wavelength of Au-WO_3 film within 1/2 h of coloring, and again after four days had elapsed after electrochemical coloring. Immediately after electrochemical coloring there is excess absorption in the IR, characteristic of pure WO_3 . At the same time, the absorption anomaly at 6000 \AA has shifted to 5500 \AA , giving rise to the red color observed. After aging while the absorption band remains centered at 5500 \AA , the film loses its excess IR absorption.

The optical density of films of various Au concentrations within 1/2 h after they had been electrochemically colored is shown in Fig. 3. When the Au concentration is near 2.8 at. %, or below, the optical absorption anomaly has been reduced to a shoulder and the IR absorption band dominates the optical properties. At lower Au concentrations, the cermet behaves like pure WO_3 .

ELECTRICAL PROPERTIES

We have found that films of Au-WO_3 with 11 at. % Au change their resistivity by 4-6 orders of magnitude upon electrochemical coloration. A typical change is from $7.0 \times 10^5 \text{ } \Omega\text{-cm}$ to $1.6 \text{ } \Omega\text{-cm}$. This is consistent with our observation of excess optical density in the IR, which is believed to be caused by electrons hopping between W^{5+} and W^{6+} sites^[8]. The metallic electrical behavior is associated with the IR absorption band.

Several hours after coloring, the resistivity of the Au-WO_3 films has increased back to its initial value although the films are still pink. The increase in resistivity begins minutes after the electrochemical coloration has been completed.

Films of Au-WO_3 have a temperature-dependent resistivity $\rho(T)$ characteristic of a whole class of composite materials^[9]. Generally, $\log \rho \propto T^{-1/2}$ in the cermets. We show such behavior in Fig. 4 for a set of colored and

as-prepared Au-WO₃ samples. The inset is a pair of measurements for a film as prepared and then again some hours after coloring. The resistivity has returned to within an order of magnitude of its starting value but the film remained pink. Note that the different slopes of the two curves indicate a change in the matrix material.

In Fig. 4 the set of data of $\log \rho$ vs $T^{-1/2}$ for the colored samples (inset excepted) was obtained within 1/2 h of coloring the samples when the resistivity was many orders of magnitude lower than that of the as-prepared samples. At about 5.5 at. % Au the temperature-dependent resistivity of the films changes character. At higher Au concentrations the colored films behave as if the matrix were insulating, whereas below 5.5 at. % Au the matrix is clearly contributing to the conductivity. At 1.8 at. % Au, the colored film is metallic, similar to that observed by Crandall and Faughnan^[5].

It should be noted that at all Au concentrations reported here, the Au grains are isolated in the WO₃ matrix and do not form a continuous pathway across the sample. When conducting metal filaments bridge the sample, the conducting behavior is dominated by the metal^[9]. Our Au-WO₃ samples have the structure of isolated grains of metal sometimes referred to as the "dielectric regime"^[9] of granular metal films.

CONCLUSIONS

We have shown that the presence of finely dispersed gold grains profoundly modifies the electrochromic properties of amorphous WO₃. When the Au concentration is above 11 at. %, no extended electronic states are created by electrochemical coloring of the samples, and the material behaves like a granular metal. When the Au concentration is below 2.8 at. %, the optical properties and the electronic properties are characteristic of electrochromic WO₃.

ACKNOWLEDGMENTS

We are grateful to J. Zelez for skillful sample preparation and to J. Pietras, S. Bozowski, and A. Pica for assistance with the measurements. We are grateful for the skills of H. Whitaker, J. McGinn, E. Bertin, and R. Paff in the materials characterization measurements.

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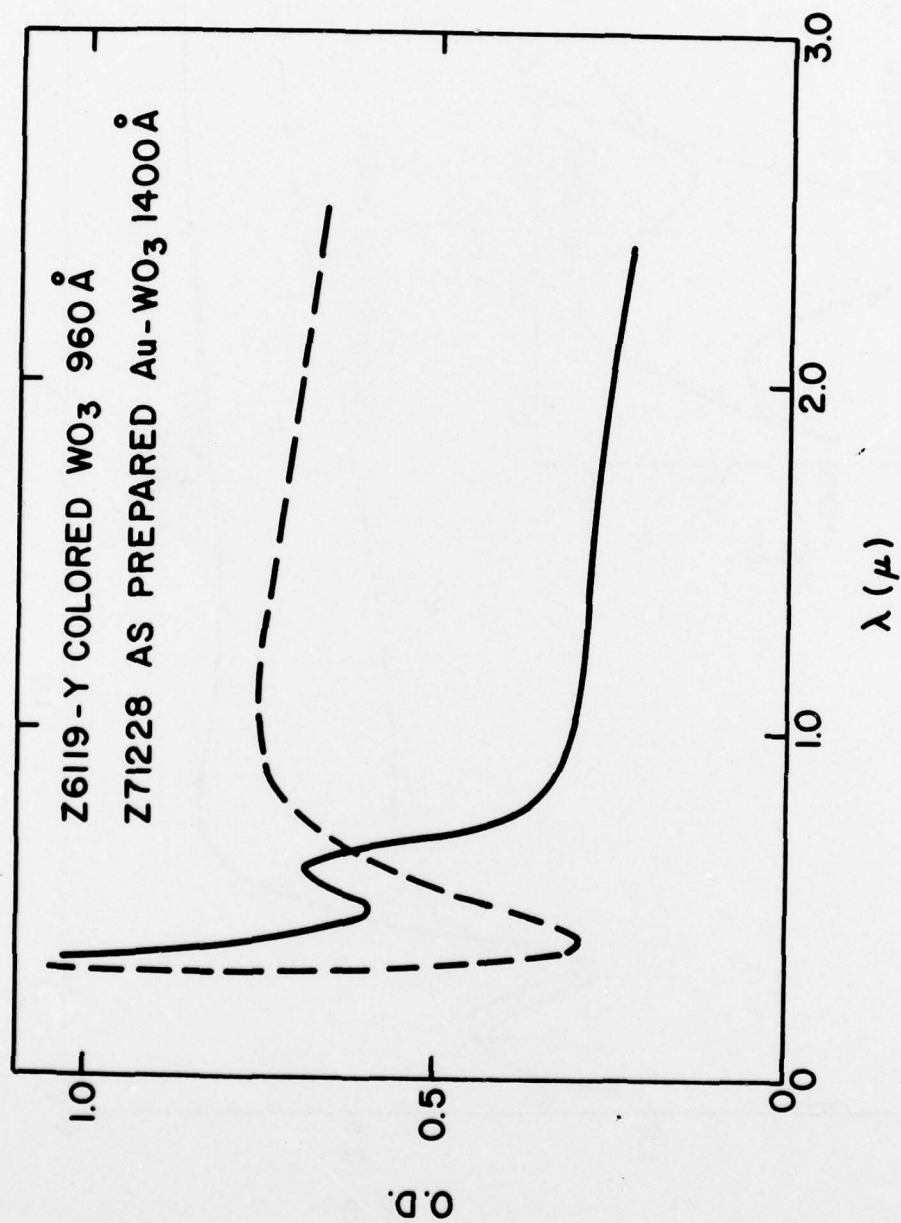


Figure 1. Optical density vs wavelength of colored WO_3 , 960 Å thick (dashed curve), and as-prepared Au- WO_3 cermet, 8.7 at. % Au, 1400 Å thick.

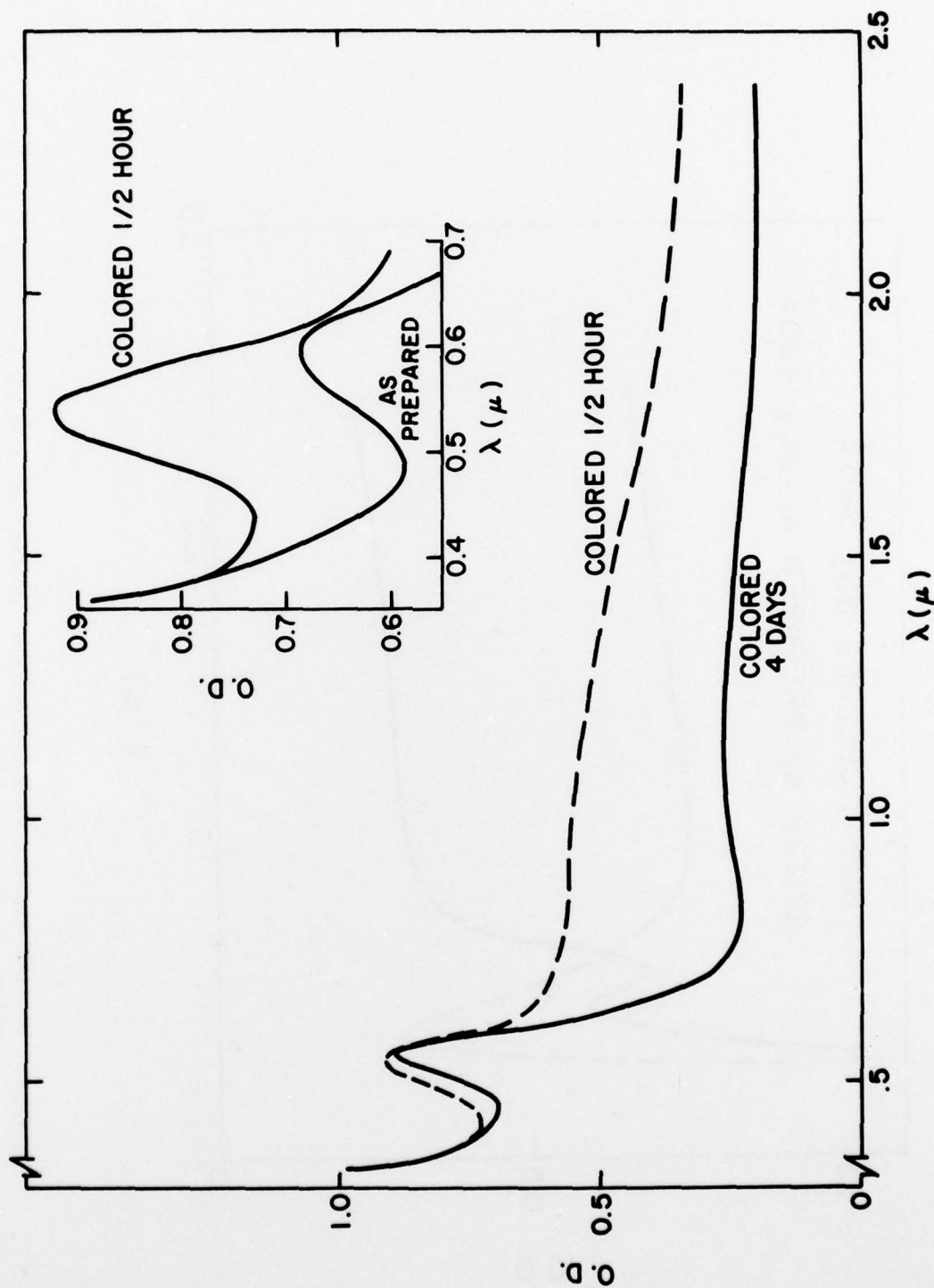


Figure 2. Optical density vs wavelength of Au-WO_3 , 8.7 at. % Au, 1400 Å thick. Dashed curve taken within 1/2 h of electrochemical coloration; solid curve taken after four days had elapsed since coloring. Insert shows the absorption anomaly at 0.6 μ for the as-prepared film and at 0.54 μ for the freshly colored film.

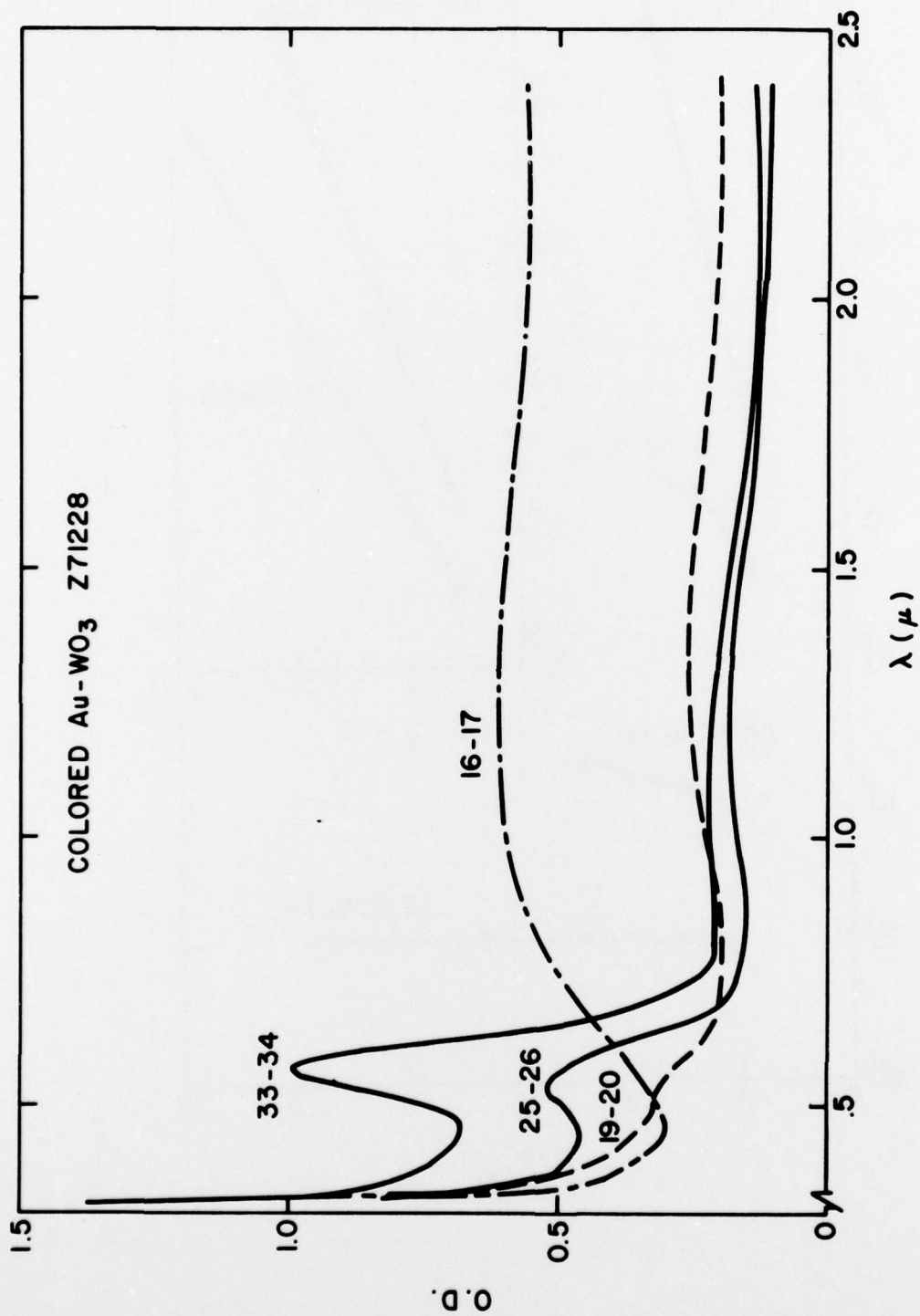


Figure 3. Optical density vs wavelength for Au-WO₃ cermet, about 1400 Å thick, at 2.8, 5.5, and 11 at. % Au within 1/2 h after electrochemical coloration.

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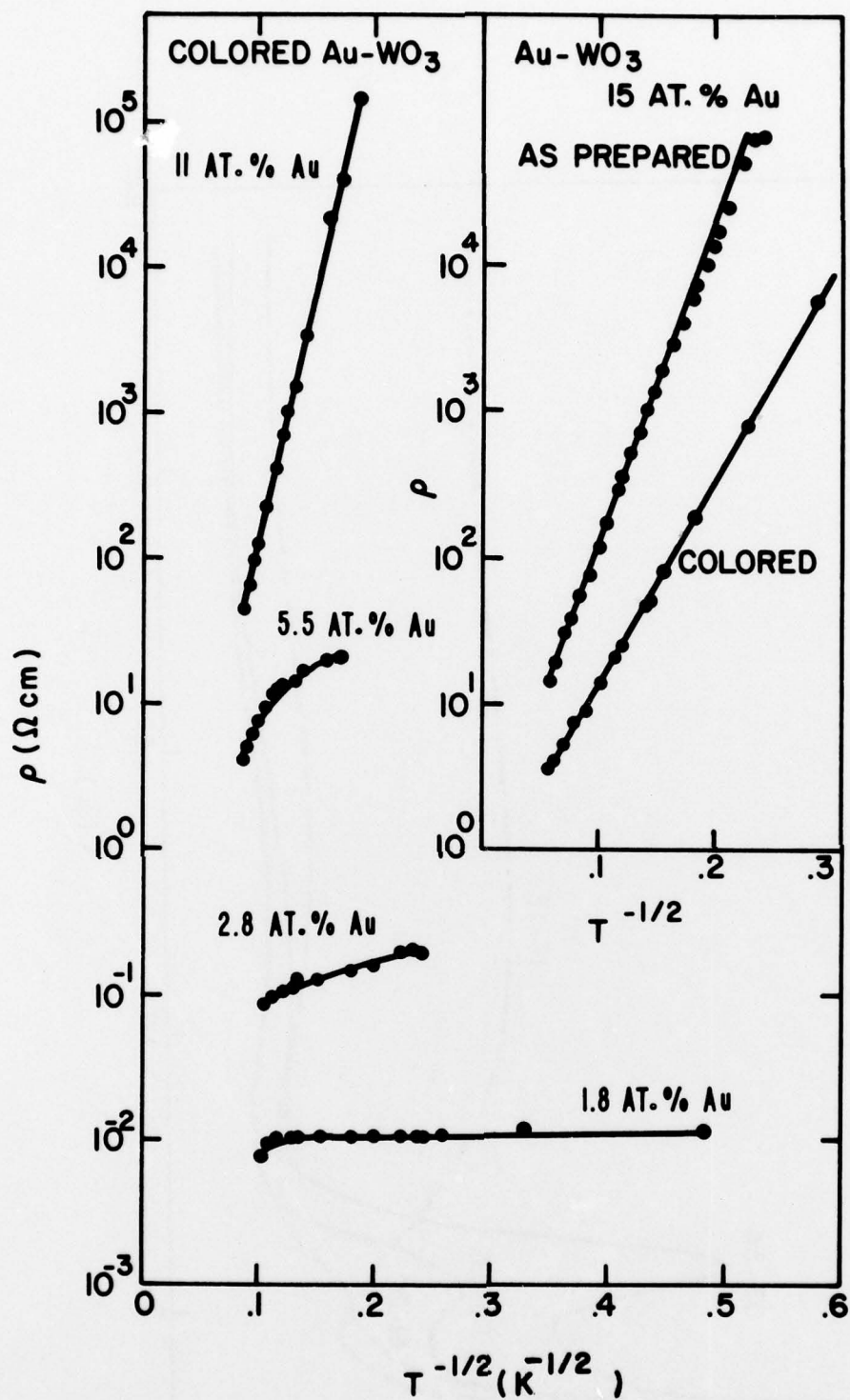


Figure 4. Resistivity of freshly colored Au-WO_3 films vs $T^{-1/2}$ for 1.8, 2.8, 5.5, and 11 at. % Au. Inset shows the resistivity vs $T^{-1/2}$ for a film as prepared and several hours after electrochemical coloration.